SELECTIVE PRODUCTION OF PROPYLENE FROM METHANOL USING MONOLITH STRUCTURED ZEOLITE AND MODIFIED ZEOLITE ZSM-5 CATALYSTS

BY

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A Thesis Presented to the

DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMICAL ENGINEERING

December 2016

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRAN- 31261, SAUDI ARABIA

DEANSHIP OF GRADUATE STUDIES

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Dedicated to:

Parents, Sister, Teachers and Friends

ACKNOWLEDGMENTS

Praise be to Allah, the Almighty, for giving me the energy that empowered me to complete this work successfully. I am thankful to Chemical Engineering department of King Fahd University of Petroleum and Minerals for providing me all the facilities during my research work.

I wish to express my deepest gratitude to my thesis supervisor, Dr. Nadhir A.H. Baghli for his valuable support and full guidance throughout the period of my research. He just not guide me in the research work but also provide me moral support during the crucial moments of my research work. I am grateful to Dr. Shakeel for his constructive ideas and suggestions during full period of my research work. I am greatly thankful to Dr. M. Mozahar Hossain for providing me his lab for the work and his valuable support.

I would like to thank Dr. Mohammad Ashraf Ali for his assistance in understanding the fixed bed reactor system, GC analysis and financial support during my research work. I would like to thank lab technician Mr. Amanullah and my colleagues specially Mr. Mohammad Haris and Mr. Sagir Ahmed for their support and help in lab work.

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LIST OF ABBREVIATIONS

BET	:	Braunauer-Emmett-Teller
DI	:	Deionized
DME	:	Dimethyl Ether
EDX	:	Energy Dispersive X-ray
FCC	:	Fluidized Catalytic Cracking
FID	:	Flame Ionization Detector
GC	:	Gas Chromatography
HC	:	Hydrocarbon
MTG	:	Methanol to Gasoline
MTO	:	Methanol to Olefins
MTP	:	Methanol to Propylene
SEM	:	Scanning Electron Microscopy
TCD	:	Thermal Conductivity Detector
TOS	:	Time of Stream
TPD	:	Temperature Program Desorption
WHSV	:	Weight Hourly Space Velocity
XRD	:	X-Ray Diffraction

ABSTRACT

Full Name : [Mohammad Nisar

Thesis Title : [Selective Production of Propylene from Methanol using Monolith Structured Zeolite and Modified Zeolite ZSM-5 Catalysts]

Major Field : [Chemical Engineering]

Date of Degree : [December 2016]

Selective production of propylene from methanol over monolith structured ZSM-5 and 'P, Ce, Fe, La' modified ZSM-5 catalysts were studied on a fixed bed reactor system. Catalytic activity of zeolites ZSM-5 with SiO_2/Al_2O_3 molar ratio of 30, 50, 80, 280 and 410 were investigated initially and it was found that ZSM-5-280 exhibit best catalyst performance. The reaction conditions were optimized and found to be temperature 500 °C, 1 bar pressure and weight hourly space velocity (WHSV) of 15 h^{-1} with methanol as feed. At optimum reaction conditions zeolite ZSM-5-280 result propylene selectivity of 47.3%, yield 17.4% with 100% methanol conversion. Best modified catalyst was obtained with 0.1 wt% phosphorus loading on ZSM-5-280 which improved propylene selectivity by 14% and yield by 24.7%. Monolith structured catalysts were prepared by single layer (6.8%), double layer (10.3%) and triple layer (13.1%) coating of ZSM-5-280 catalyst. ZSM-5-280 single layer monolith coated structured catalyst effectively increased propylene selectivity by 19.2% and yield by 34.5%. This effective change is due to better internal diffusion and

reduction in mass transfer resistances in monolith channels which causes short residence time and hence reduces aromatics by decoupling of intrinsic reactions and increases olefins.

Analytical techniques such as XRD, SEM-EDX, BET and NH_3-TPD were applied to investigate physical and chemical characteristics of pelletized parent, P-modified and prepared monolith structured ZSM-5-280 catalysts. The NH_3-TPD results reveal that the acidity decreases with increase in SiO_2/Al_2O_3 molar ratio of ZSM-5 catalysts. Acidity of P-modified ZSM-5-280 catalyst reduced by 43.0% due to partial elimination of strong acid sites. The XRD pattern obtained for monolith structured catalyst confirmed the presence of washcoat on monolith structured support. The SEM images of P-modified and monolith structured ZSM-5-280 catalysts confirmed that there is no change in crystallinity of ZSM-5-280 catalyst. SEM images revealed a uniform catalyst coating inside the channels of monolith structured support.

ملخص الرسالة

الإســم: محمد نثار

عنوان الرسالة: *الإنتاج الاختياري لمادة البروبلين من الميثانول باســـتخدام حفّاز الزيولايت ZSM-5 متراص الهيكلية.*

التخصص: الهندسة الكيميائية

تاريخ التخرج: ديسمبر 2016م

تمت دراسة إنتاج انتقائي للبروبيلين من الميثانول باستخدام هيكلة متراصة لـــZSM-5. في ذلك، تم استخدام P ،Ce ،Fe و La كحفازات ZSM-5 على نظام مفاعل ســـرير ثابت. وقد تم في البداية التحقيق في النشـــاط الحفزي للزيوليت ZSM-5 مع نسـبة جزيئية SiO_2/AL_2O_3 30، 50، 80، 280 و 410، حيث وجد أن ZSM-5-280 يظهر أفضل أداء كمحفز. تم البحث في ظروف التفاعل لنستنتج أن أفضلها كان في درجة حرارة 500 مئوية، و ضغط 1 بار و سرعة تدفق وزنية 15 1/ساعة مع الميثانول كعلف .في أفضل ظروف التفاعل أنتج الزيوليت ZSM-5-280 الانتقائية 47.3%، و الانتاج 17.4 % للبروبيلين مع تحويل الميثانول بنسـبة 100%. تم الحصـول على أفضـل حافز باسـتخدام نسـبة 0.1% من وزن الفوسـفور محملا على ZSM-5-280 مما أدى إلى تحسـن انتقائية البروبيلين بنسـبة 14% و انتاج بنسبة 24.7 %. تم تحضير الحفازات ذات الهيكلية المتراصة من طبقة واحدة (6.8%)، طبقة مزدوجة (10.3%) و طبقة ثلاثية (13.1%) من الطلاء ZSM-5-280 حافزا. الحفازات المطلية بطبقة واحدة زادت الانتقائية للبروبيلين بنسبة 19.2% الانتاج بنسبة 34.5%. هذا التغير الفعلي سببه النشر الداخلي الأفضل والحد من مقاومة نقل الكتلة في القنوات المتراصـــة، مما يسـبب وقت إقامة قصـيرة وبالتالي يقلل من المركبات المتطايرة عن طريق فصـل التفاعلات الجوهرية وزيادة الأوليفينات.

تم تطبيق تقنيات تحليلية مثل XRD، SEM-EDX، BET و NH_3-TPD للتحقيق في الخصـــائص الفيزيائية والكيميائية لكل من الحفازات النقية المطلية، والمعدلة بالفسـفور والمحضـرة بهيكلة متراصـة ZSM-5-280. تكشـف

نتائج NH_3-TPD أن الحموضة تتناقص مع زيادة في النسبة الجزيئية SiO_2/AL_2O_3 لحفازات ZSM-5. تم خفض حموضة ZSM-5-280 المعدل بالفسفور حافزا بنسبة 43.0% وذلك بسبب القضاء الجزئي على مواقع الحمض قوية. .انماط XRD التي تم الحصـــول عليها للحافز ذو الهيكلية المتراصـــة ZSM-5-280 أكدت عدم التغير في تبلور الحافز. وكشفت صور SEM طلاءا حافزا ذا نمط منتظمٍ متساوٍ داخل قنوات متراص الهيكلية.

درجة الماجستير

جامعة الملك فهد للبترول والمعادن

الظهران، المملكة العربية السعودية

ديسمبر 2016م

CHAPTER 1

INTRODUCTION

1.1 Background

Ethylene and propylene are light olefins and its market is mostly focused on polymers and fiber industries. Ethylene is the main consumed chemical by volume while Propylene is an important feedstock for polypropylene, propylene-oxide acrylonitrile, phenol and many other chemicals. Use of propylene extends over various industries such as automotive, construction, packaging, medical and electronics. Due to increase in demand of propylene, its price is also increasing. Worldwide most of the olefins are produced by thermal cracking of naphtha, or other light fractions of petroleum with steam cracking [1], a new production technology from renewable resources such as methanol can be realized using zeolite based technology. The production of olefins from methanol is known as methanol to olefins (MTO) process. The product ratio of ethylene and propylene is influenced by the operating conditions of the reactor mainly by temperature and pressure. The conversion of methanol towards propylene can be targeted using selective catalysts such as ZSM-5 and SAPO-34, ZSM-5 gives the best results due to its morphology. It is expected that metals and semi-metals modified ZSM-5 catalysts will improve the selectivity towards propylene and also it will be more water tolerant at high temperature and pressure, exhibit slow deactivation and show high mechanical strength. We are proposing a study for

the development of various metals and semi-metals modified and monolith structured zeolite catalyst for the catalytic conversion of methanol into light olefins mainly 'Propylene'. Figure 1.1 reflects the global demand of propylene by the year 2020 and it is clear from the figure that it will increase by a huge number in the near future.

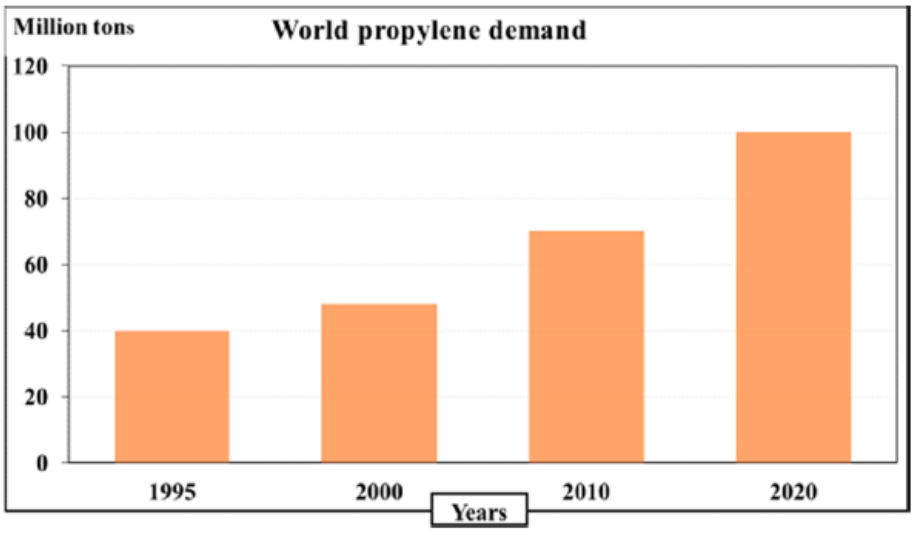


Figure 1.1 Global demand for propylene [2].

Worldwide ethylene market is likely to reach US$234.2 billion by the end of the year 2020, growing at 6% CAGR from 2014 to 2020 [3]. Worldwide ethylene is produced by petrochemical companies, due to its wide industrial applications. Production volume of ethylene increased periodically, in petrochemical companies due to its growing response for ethylene from several end-use manufacturers which leads to sustainable progress of the international ethylene market. Polyethylene is the main end use product holding more than 50 percent of the ethylene market by the end of 2015. A variety of polyethylene are consumed in the production of plastics, which further are used in making of everyday usages, packing material, pipes, and toys [3]. Plastics formed of polyethylene can be utilized into different shapes including simple and complex. In 2011, worldwide propylene market

was worth more than 90 billion US dollar which is expected to exhibit substantial development in the coming years. Propylene is consumed mainly in the manufacture of propylene polymers which have many applications including acrylic fibers coatings, polyurethane resins, PVC plasticizers, epoxy resins and polycarbonates and solvents. The automotive sector is the major end user of polypropylene. Huge development in the production of ethylene and propylene which are shared with growing response in place of downstream products from India, China, and the Middle East, will push growing overall ethylene and propylene market. Severe environmental rules and regulations differences in the prices of raw material and political uncertainties in crude oil producing regions are major issues warning the ethylene and propylene market.

In the thermal cracking process of naphtha, the yield of ethylene is around 33% while propylene is 17%. High energy requirement, lack of selectivity, coke formation are the drawback of these routes [2], [4]. An alternative route is to convert Methanol to propylene i.e. MTP. Methanol is the most important chemical produced worldwide in huge amount and is cheaply available all around the world, so its conversion to propylene is alternative to thermal cracking process. UOP claims a return on investment of 25%/year, as compared to 15% for a thermal naphtha cracker.

MTO process to be applied for expansions of existing olefins plants, it is a well-known fact that the choice of the catalyst favors the yield of either ethylene or propylene. A process should be selected that responds to the local needs where there may be a shortage of either ethylene or propylene. Two main processes available are UOP/Norsk Hydro using SAPO-34 catalyst and Lurgi/Statoil using a ZSM-5 catalyst claiming high propylene yield [5]. In both cases, the temperature is in the range of 450-500°C. A catalyst is a substance

that accelerates the progress of a chemical reaction towards equilibrium and allows the reaction to occur with a low energy barrier. A catalyst does not change the thermodynamics (energy difference between starting materials and products) and the equilibrium concentrations of a reaction. Figure 1.2 shows potential energy diagrams of catalytic and non-catalytic reactions. The non-catalytic reaction path goes through a much higher energy barrier. Catalysis is divided into three categories i.e. homogeneous, heterogeneous and biocatalysts (enzymatic) [4]. In homogeneous catalysis reactants, products and catalyst are in one phase, usually in the liquid phase while in heterogeneous catalysis reactants, products and catalyst are in unlike phases. Typically, the catalysts are solid while the reactants and products are gasses or liquids. Various zeolites catalysts are used for a wide range of industrial applications due to their unique properties. The success story of converting methanol to propylene commercially was achieved during the period of the 1990s, since then the increase in demand for propylene is the cause of developing a noble catalyst which can increase propylene selectivity in MTP reaction. Chang and Sivestri used acidic zeolites to convert methanol to hydrocarbons in the year 1977 [6]. Based on the product distribution Zeolites Silicoaluminates ZSM-5 and Silicoaluminophosphates SAPO-34 are most commonly used catalysts in MTO process [7]. The zeolite can be prepared by considering compositions, acidity, and structure of catalysts. In the recent time nano zeolites have also shown their importance due to the presence of large surface area and mesoporosity [8].

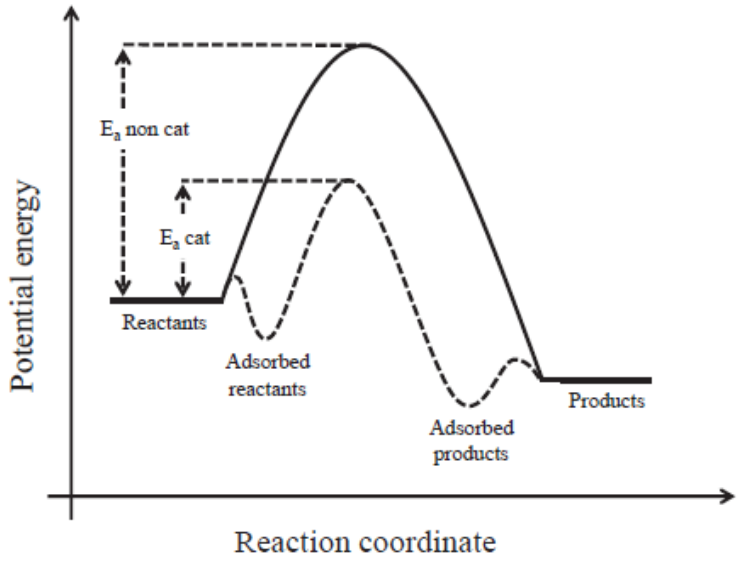


Figure 1.2 Potential energy diagram for non-catalytic and catalytic path [9].

The Zeolite catalysts are crystalline aluminosilicates with a three-dimensional structure that consists of nanometer-sized channels and cages resulting in a high porosity and a large surface area [10]. Figure 1.3 shows three-dimensional framework of zeolites ZSM-5 and SAPO-34 catalysts which are used in MTP process. The dimensions of zeolite channels, channel intersections, and/or cages are typically less than 2 nm. IUPAC classifies porous materials as microporous, mesoporous and macroporous based on sizes < 2 nm, 2-50 nm and > 50 nm respectively [11], zeolites are referred to as microporous materials.

SiO_2/Al_2O_3 molar ratio of a ZSM-5 catalyst is an important parameter and affects the product distribution in MTP process. Decrease in SiO_2/Al_2O_3 ratio of ZSM-5 catalyst led to increase in both strong and weak acid sites and increase in SiO_2/Al_2O_3 ratio led to decrease in strong and weak acid sites [7]. Crystal morphology, acidity and BET surface area are influenced by SiO_2/Al_2O_3 ratio of zeolite ZSM-5 catalyst. High SiO_2/Al_2O_3 ratio ZSM-5 catalysts having moderate acidity are considered suitable for high propylene yield in MTP process [7], [12].

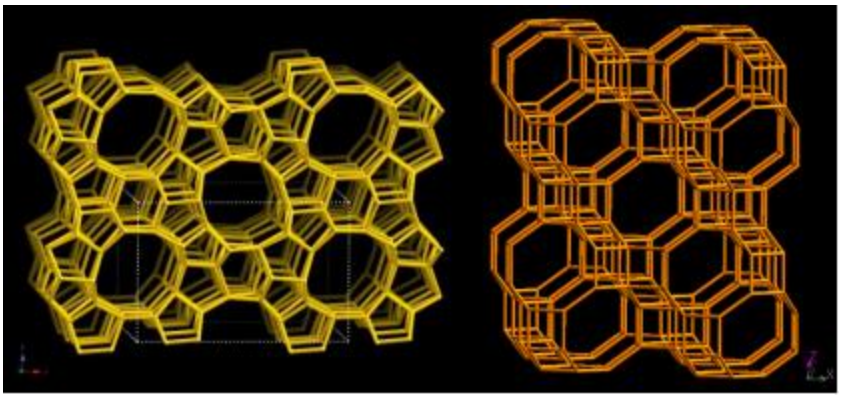


Figure 1.3 Framework structure of ZSM-5 and SAPO-34 catalysts [13].

Catalyst modification by promoters is an effective way of modification of zeolite catalysts which result in better catalyst performance. In MTP reaction the weak acid sites are important and are regarded as the active sites for olefins production. Weak acid sites play an important role in reducing the formation of alkanes and aromatics, it also provides better stability and anti-coking capability than the strong acid sites in MTP reaction. It is well-known fact that the side reactions on active sites cause the coke formation which results in deactivation of active sites with the continuous reaction time. The ZSM-5 catalysts life is enhanced by the presence of weak acid sites instead of strong acid sites due to reduced coke formation. Since the acidity plays an important role in MTP reaction, therefore, it is important to control the relative quantity of weak and strong acid sites for better results. Promoters are doing the same and also they provide extra acid sites on the surface and enhance the performance of catalysts. Loading of the suitable promoter [12], [14], [15], renovation of mesopores [16] to ZSM-5 results in high propylene selectivity and better catalyst performance due to modification in acidity and porosity. Promoters not just eliminate the strong acid sites but also helps in reducing the aromatics formation. In this work modification on zeolite catalyst was done by using Ce, Fe, La and P promoters.

Structured catalysts are introduced to obtain better results in MTP process. In recent year's high thermal conductivity and better mechanical strength materials are used to develop this kind of catalyst having many parallel channels. Structured catalysts have crucial advantages for better mass and heat transfer, low-pressure drop and contact time due to shorter diffusion distance and faster intra-diffusion rate of both reactants and products. These advantages are key factors for replacing fixed bed reactors by structured catalysts reactor. The three-dimensional structure alters the mass and heat transfer properties. High cell density and the thinner wall of structured catalyst exhibits maximum conversion and propylene selectivity in MTP process [17]. Monolith reactor is most widely used structured catalytic system [18]. In our study, we use ceramic cordierite honeycomb monolith (14 wt% MgO, 36 wt% Al_2O_3 and 50 wt% SiO_2) [19]. The best catalyst obtained in the study was coated on the monolith by dip coating method [20]. Monolith structured catalysts were prepared by a single layer, double layer and triple layer coating of zeolite. The increase in coating thickness causes a negative effect on methanol conversion and propylene selectivity due to diffusion limitation in the intra pores of catalysts wall [17].

In the past decades, numerous works have been published on methanol-to-hydrocarbons conversion process but the focus was mainly on the production of propylene from methanol was the apprehension.

The overall reaction path may be represented [6] by equation 1.1 below:

$$\frac{n}{2}[2CH_3OH \rightarrow CH_3OCH_3 + H_2O] \xrightarrow{-nH_2O} C_nH_{2n} \quad \rightarrow \quad n[CH_2] \quad ---(1.1)$$

Methanol DME Water Olefins Paraffins + Aromatics

The nature of reaction for methanol conversion to olefins is autocatalytic and the reaction steps are kinetically coupled generally. Distribution of various products in MTP are influenced by the properties of catalyst and different reaction parameters such as temperature, pressure, space velocity. Figure 1.4 shows different products obtained during MTO reaction over a zeolite catalyst.

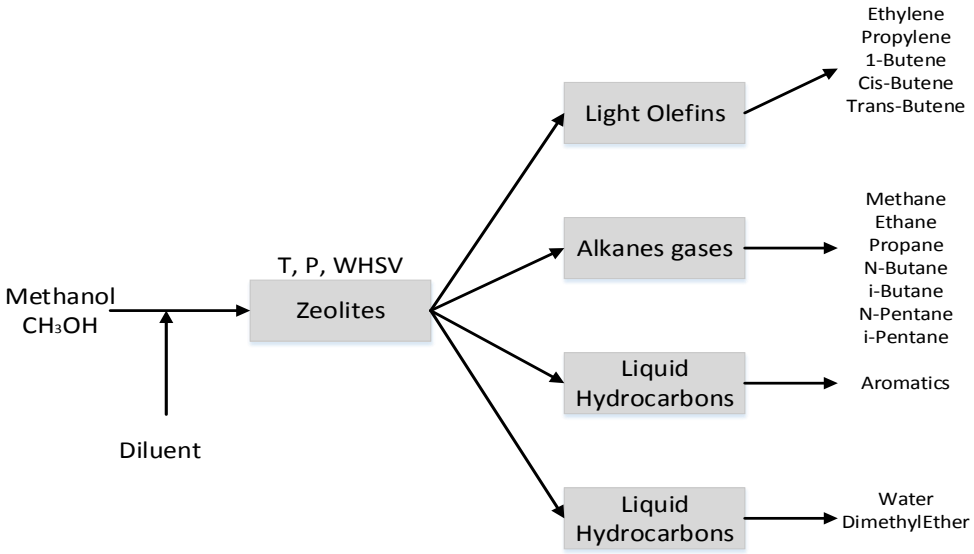


Figure 1.4 Methanol Conversion Reaction Scheme.

1.2 Research Strategy

The focus of the thesis is to study the conversion of methanol to propylene using ZSM-5, modified ZSM-5 and monolith structured ZSM-5 catalysts. Emphasis was given to the catalyst activity and selectivity. Experiments were carried out in a fixed bed reactor with continuous methanol feed. To do this initially ZSM-5 zeolites with SiO_2/Al_2O_3 ratio of 30, 50, 80, 280 and 410 were characterized and evaluated on fixed bed reactor. The best catalyst obtained in terms of SiO_2/Al_2O_3 ratio for maximum methanol conversion and propylene

selectivity than further modified by using several promoters i.e. phosphorus, cerium, iron and lanthanum and evaluated on the reactor system. Loading of promoters was optimized on this catalyst. The best catalyst in terms of SiO_2/Al_2O_3 ratio was coated on macroporous monolith structured support by dip coating method and tested on reactor system at optimized reaction conditions. Best modified and monolith structured catalysts were characterized for acidity, EDX analysis, BET surface area and SEM for surface morphology. The stability of parent, modified and monolith structured catalysts were also studied based on the long run.

To achieve this target of research work a fixed bed reactor system with online GC7890B (TCD and FID) was installed in the beginning and commissioned according to the requirements of methanol to propylene reaction system. In the first step characterization of ZSM-5 zeolite catalysts with SiO_2/Al_2O_3 ratio of 30, 50, 80, 280 and 410 were carried out, especially EDX analysis for elemental compositions. Testing of catalyst samples was carried out in a fixed bed flow reaction system attached with online GC (FID-TCD) for analyzing the gaseous and liquid products obtained in MTP process. Effect of temperature, pressure, feed flow rate i.e. WHSV was also studied for these catalysts. Optimum reaction conditions were obtained, other parameters like the ratio of catalyst amount vs SiC, Inert N_2 vs feed flow rate and water temp of chiller were also studied for better results.

In the second part of the work hydrothermally and mechanically stable cordierite honeycomb monolith with 400 CPSI was selected for coating of zeolite catalyst on the monolith. The coating was a critical part of the experimental method, to do this dip coating method was used to make sure that the coating should be uniform, coated monolith catalyst was dried and calcined to remove excess wetness and any kind of impurity. ZSM-5 coated

monolith structured catalyst was characterized and evaluated in the fixed bed flow reactor at optimized reaction conditions.

In the third part of the analysis modification of best obtained ZSM-5 catalyst was done using promoters Fe, Ce, La and P by incipient impregnation technique. The amount of loading was optimized, samples were characterized and tested on the reactor system for maximum methanol conversion and propylene selectivity.

1.3 Objectives of the Study

The main objective of this study is to enhance propylene selectivity and yield at high methanol conversion using modified ZSM-5 and monolith structured ZSM-5 catalysts.

The detailed objectives of the study are as follows:

1. Evaluation of ZSM-5 catalysts with SiO_2/Al_2O_3 ratio of 30, 50, 80, 280 and 410 on a fixed bed reactor system for maximum methanol conversion and propylene selectivity.
2. Optimization of process variables temperature, pressure and WHSV for high propylene production with maximum methanol conversion.
3. Modification of best zeolite catalyst using various promoters, evaluation of these samples on reactor system to get best-modified zeolite catalyst for maximum methanol conversion and propylene selectivity.
4. Coating of the best zeolite ZSM-5 catalyst obtained in the study with different layer by dip coating method and evaluation in the reactor system for catalytic activity.
5. Characterization of parent, modified and monolith coated zeolite catalyst samples for physical and chemical properties.

6. Catalytic performance evaluation based on a long run with time to compare the performance of best ZSM-5, best-modified ZSM-5 and monolith structured ZSM-5 catalysts.

CHAPTER 2

LITERATURE REVIEW

2.1 History

In chemistry, we define an olefin as an unsaturated chemical compound containing at least one C=C bond. Olefins have sigma and pi bonds, it is the presence of these pi bonds that makes olefins special. Most reactions of olefins involve breakage of the pi bond. Olefins are fundamental building blocks for many end products mainly polymers. One of the widely used olefins is propylene. It is an important feedstock used to produce polymer intermediates and chemicals, some important derivatives of propylene are polypropylene, acrylonitrile, cumene, phenol, isopropyl alcohol, propylene oxide. Figure 2.1 shows the end products that can be obtained from propylene. Propylene demand is increasing worldwide mainly in Asia pacific region. Presently, polypropylene consumes 62% worldwide propylene production and it will increase in the future [21].

The majority of the light olefins in today's world are produced by thermal cracking either by steam cracking of light hydrocarbon liquids/natural gas or catalytic cracking method [22]. In the refinery, propylene normally obtained as a by-product of gasoline production from large FCC units. Steam cracking and FCC methods are insufficient to meet the rising demand of propylene because these routes rely heavily on the catalytic transformation of petroleum hence creating a gap between supply and demand of propylene which can be

fulfilled by on-purpose technologies. On purpose processes mainly include propane dehydrogenation, metathesis, olefins cracking and methanol to olefins.

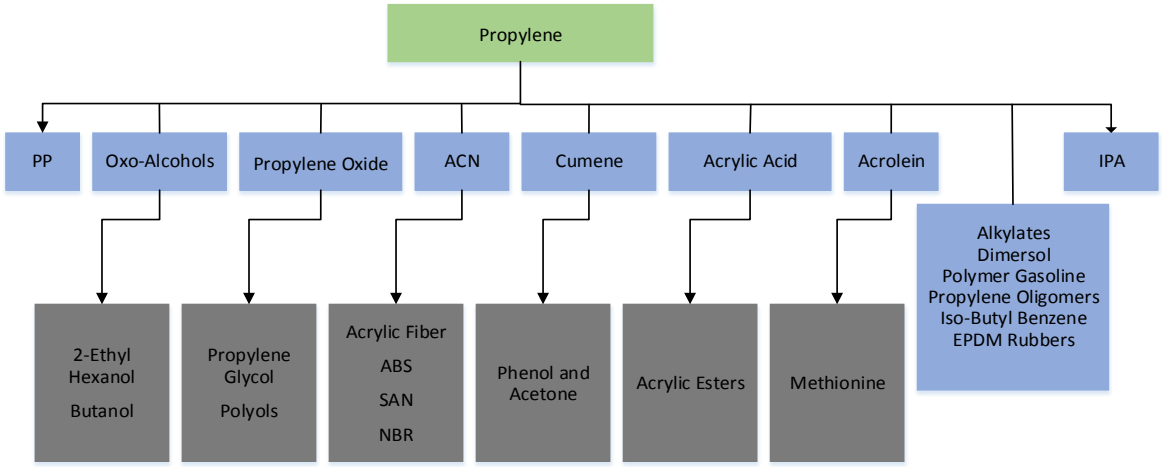


Figure 2.1 Propylene end products.

Ethylene and Propylene are also manufactured from NG, coal/HC sources. By partial oxidation method feedstock can be converted to syngas to methanol and then finally transformed to light olefins in a process such as UOP's MTO process [22]. Figure 2.2 shows the routes for the manufacture of light olefins. Currently, about 70 percent of the world's propylene, is provided by co-production from steam cracking of naphtha while 30 percent is brought as a by-product from FCC units. Visbreaking and coking in the refineries are the other sources of propylene. Propylene in any of the routes shown in Figure 2.2, is produced as a dilute stream in propane in which propane/propylene ratio varies considerably depending on process/feedstock/operating conditions and the catalysts.

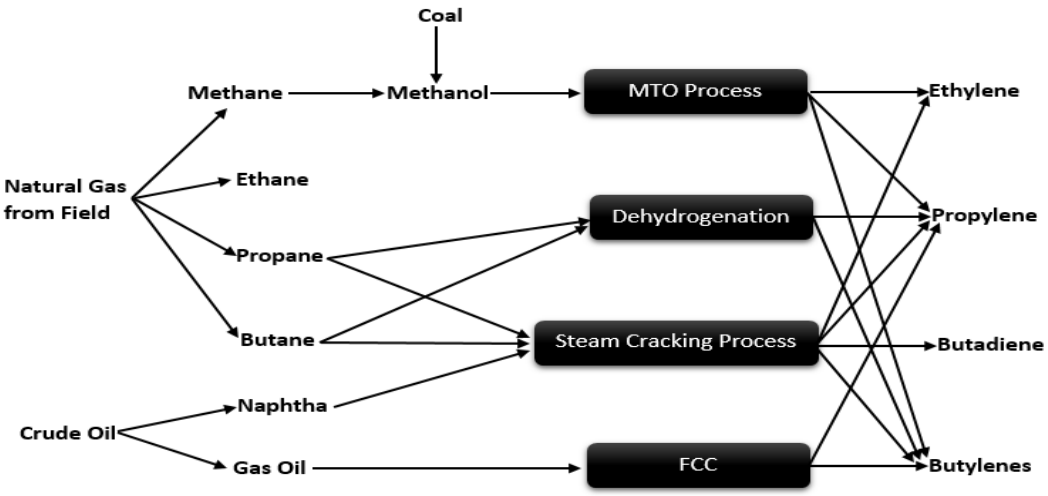


Figure 2.2 Routes for production of Olefins.

Production of olefins from non-oil based technology has been a widely researched area. Methanol can be used as feed for the production of olefins, this was initially realized by the research team of Mobil when they used zeolite for the production of high octane gasoline from methanol but got series of HC's [10], [23], [24]. Conversion of methanol to propylene is an interesting process because it produces gasoline, an important fuel as a byproduct. The first big oil crisis created in 1970's inspired a strong development in the MTH process, which played an important role in the production of synthetic fuels and other chemicals based on non-petroleum route [10], [25]. MTH technology makes it possible to produce anything which is coming from crude oil. Mobil built its first MTG plant in New Zealand, commercialized in 1985 with 14500 barrels a day production capacity (30% country's need) of gasoline from abundant natural gas resources there [26]. In this plant, methanol was used as feed to convert it into HC's using medium pore zeolite ZSM-5 catalyst [24]. The MTG and MTO processes are the family expansion of MTH process depending on the end products either gasoline or olefins. Mobil fixed bed reactor used zeolite ZSM-5 catalyst in MTG reaction with temperature 673 K and pressure several bars, and these

reaction conditions favor more paraffins and aromatics formation [25], [26]. The chemistry of MTH process has been studied using zeolites for over decades and depending on the catalyst topology and process parameters a wide range of product distribution can be obtained during the MTH reaction. The catalytic conversion of methanol leads to several articles and patent on zeolite catalysts particularly for MTO process due to the huge demand of olefins worldwide. Figure 2.3 reflects Mobil typical MTG, MTO, MOGD process. As in Figure 2.3 it can be seen that coal can also be used as an initial feed which is gasified to produce syngas which is then converted to methanol which is further used as feed for the production of olefins and gasoline by MTO and MTG processes.

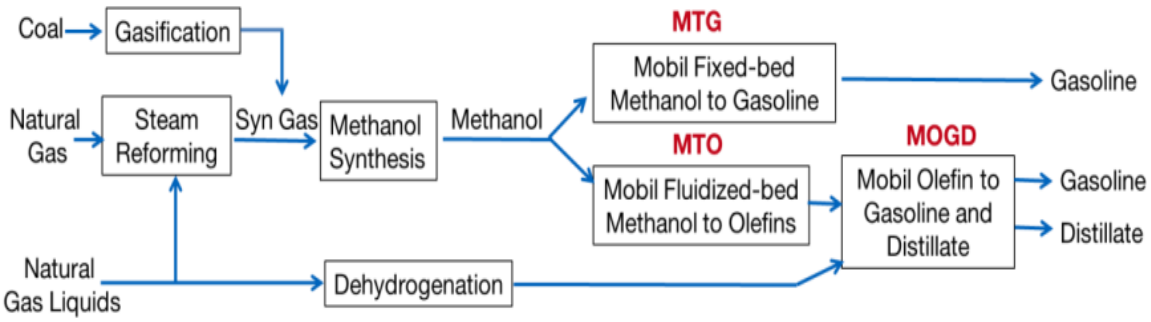


Figure 2.3 Mobil's MTG, MTO, MOGD processes [10], [25].

Another MTO process was developed in 1990 by UOP with Norsk Hydro using a SAPO-34 catalyst in a low pressure fluidized bed reactor shown in Figure 2.4 [27]. This process converts methanol to light olefins mainly ethylene and propylene. This catalyst prevents the formation of large olefins due to restrictions provided by the pore channels of the catalyst. Lurgi's Methanol to Propylene process uses a ZSM-5 catalyst to produce propylene in yields as high as 70% in a series of adiabatic fixed bed reactors that operate at a temperature of about 500 °C and at relatively low pressure. The Lurgi MTP process has been demonstrated in collaboration with Statoil in an 8000 hour pilot plant run and a commercial MTP plant constructed in china.

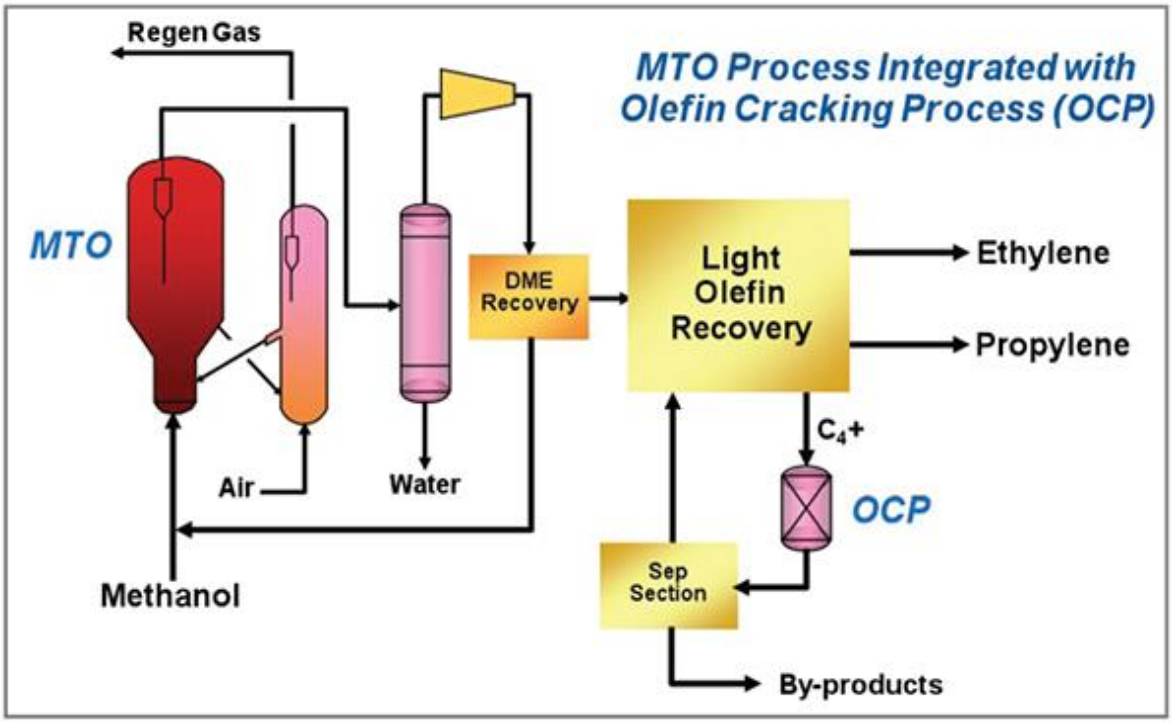


Figure 2.4 UOP/Norsk Hydro MTO process developed in 1990 [28].

2.2 Catalysts development

This section highlights the catalysts involved in methanol conversion to propylene, the effect of shape selectivity and acidity of zeolites, catalyst deactivation and some important applications of zeolite catalysts in industrial processes.

2.2.1 Zeolites

In MTP process zeolites are the main catalyst employed. Zeolites are porous crystalline aluminosilicates composed of AlO_4 and SiO_4 tetrahedral interconnected through shared oxygen atoms forming a three-dimensional network [29]. The framework structure having well-defined pore geometries enclose cavities which permit the reactant to diffuse

inside. The pore size ranges from 5-20 Å. The crystallographic unit cell is generally represented as:

$M_{x/n}\,[(AlO2)_x\,(SiO_2)_y].zH_2O$

Where:

M= cation of valence n

Z= Number of molecules of water of hydration

X= Number of AlO_2 molecules

Y= Number of SiO_2 molecules

y/x generally ranges between 1-5

Based on the product distribution Zeolites Silicoaluminates ZSM-5 and Silicoaluminophosphates SAPO-34 are most commonly used catalysts in MTO process [7]. The well-defined pores and channel structure of zeolite is its unique property which is responsible for the product distribution in MTP process i.e. it will decide the selectivity of olefins, paraffins and aromatics. This unique property of zeolite is termed as 'shape-selectivity'. Shape selectivity can be reactant selectivity, transition shape selectivity and product selectivity. Reactant selectivity simply means that pore size of zeolite will permit only a class of molecules to penetrate inside the pore channels of the zeolite catalyst. Product selectivity means that the zeolite pores will decide the de-penetration of products from the intra pores of zeolite catalyst [30].

The catalytic activity of a zeolite catalyst is defined by the presence of acidic groups within the pores i.e. intra-crystalline surface [31]. This acidic strength of a zeolite catalyst is controlled either during catalyst preparation or after catalyst preparation by certain means. Control of acid addition during catalyst preparation or addition of promoters by means of

impregnation, ion exchange, precipitation are some techniques by which acidic strength has been controlled in zeolite catalyst. Depending on the framework structure formed by SiO_4 and AlO_4 in zeolite catalysts the pore channels and cavities can have various diameters. The catalytically most important classes of zeolites are those who have 8-, 10-, 12-ring of oxygen atoms. Figure 2.5 shows pore structures of common zeolites used in industries.

Methanol to propylene or hydrocarbons is catalyzed mainly by acidic forms of the various narrow pore (8-ring), medium pore (10-ring or pentasil type), and wide pore (12 ring) zeolites. Chen and Garwood [32] and Langner [33] reported works on various aspects of shape selectivity of zeolites with different pore structures.

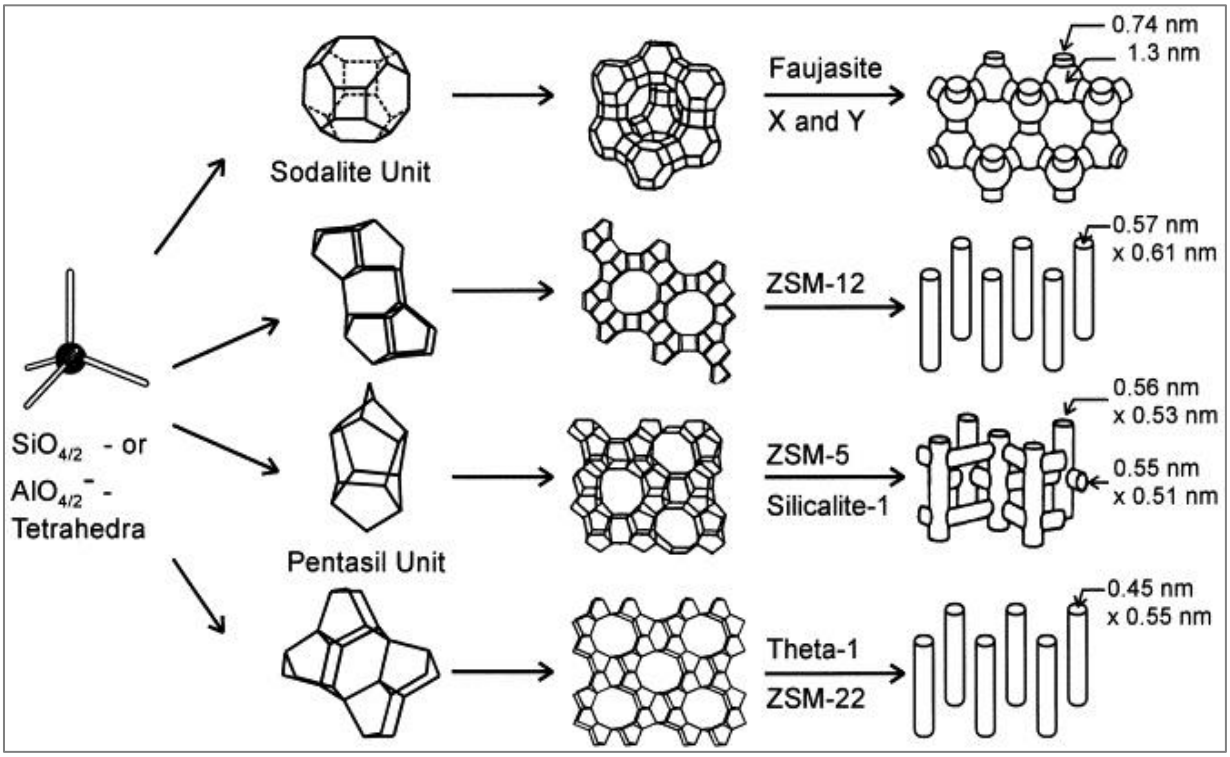


Figure 2.5 Structures of four zeolites and their micropore systems and dimensions [34].

The zeolite can be prepared by considering compositions, acidity and structure of catalysts. In the recent time nano zeolites have also shown their importance due to the

presence of large surface area and mesoporosity [8]. SAPO-34 produces both Ethylene and Propylene and some other by-products however, the catalyst has similar coke selectivity to FAU catalysts used in FCC. ZSM-5 has lower coke selectivity and produce propylene as a major product and also produces C4+ hydrocarbons.

2.2.2 Shape Selectivity and Acidity

Zeolite catalysts have a unique property known as shape selectivity. Three types of shape selectivity have been observed in zeolite catalysts these are (a) Reactant shape selectivity, (b) Product shape selectivity and (c) Transition shape selectivity. Reactant shape selectivity simply means zeolite allow to penetrate only that reactant whose size is smaller than the pore size of the zeolite catalyst. These three shape selectivity has been shown in Figure 2.6.

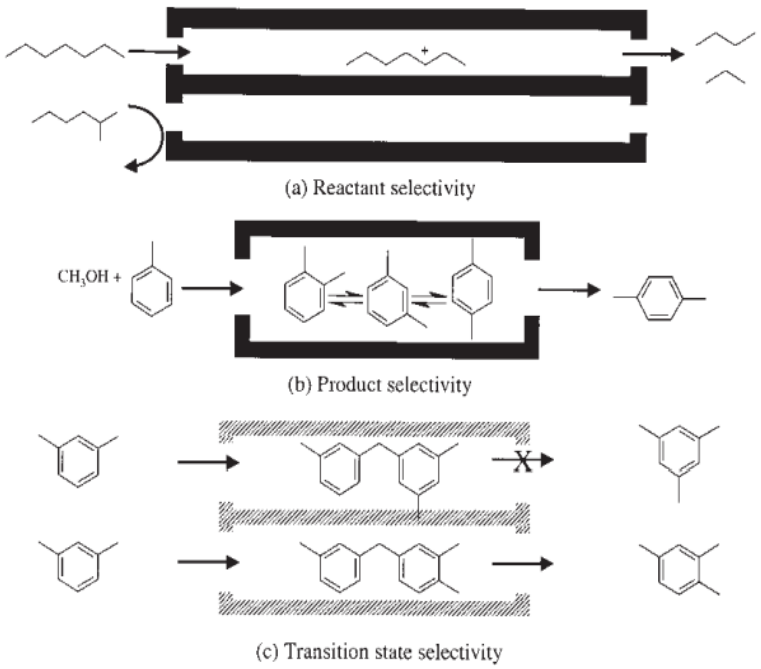


Figure 2.6 Three types of shape selectivity (a) reactant shape selectivity (b) Product shape selectivity (c) transition state shape selectivity.

Product shape selectivity means zeolite catalyst allow only those products to diffuse out of the channels whose size is smaller than the pore size. It will now allow the products to diffuse through the molecular dimension pores whose size is too large. In transition state selectivity zeolites channels behave as confined reactors. They have the steric geometrical restrictions on the transition state and the products selectivity depends on zeolite structure, crystal size and activity.

Among various important properties of the zeolite catalyst, one of the most important property is their acidity. The presence of trivalent Al zeolite framework presents a negative charge. Because of this behavior zeolites serve as Bronsted acids and widely used for acid catalyzed reactions [35]. The presence of other sites shown in Figure 2.7 act as Lewis acid sites, in this Al behaves as an electron acceptor.

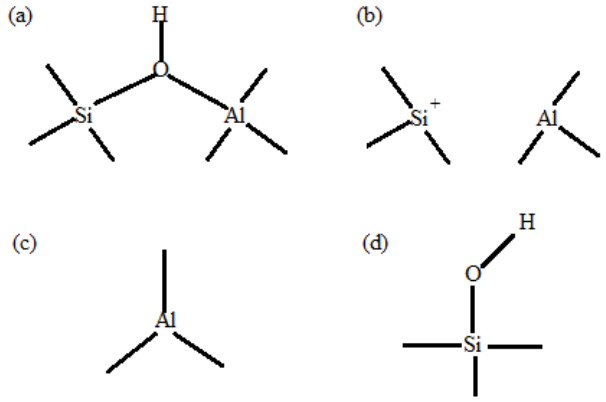


Figure 2.7 Acid sites in zeolite (a) Bronsted acid site, (b) Lewis acid site.

2.2.3 Catalyst Deactivation

The deactivation of a zeolite catalyst is normally due to coke formation. Generally, the rate of deactivation in SAPO-34 is faster than ZSM-5 catalyst [36]. Faster deactivation is the results of high aromatics and heavy branched paraffins formation during the reaction.

These molecules cannot easily diffuse out of the pores of zeolite catalysts and cause carbonaceous deposits inside the catalyst pores. The operating conditions play an important role in the catalyst deactivation. Water introduction in the methanol feed helps in less coke formation and hence improve the life of the catalyst. The high temperature is suggested in MTP process. Catalyst modification by promoters helps in reducing coke formation due to decrease in Bronsted acid sites responsible for aromatics and paraffins formation in MTP reaction [37]. Structured catalyst deactivation by coke generation is slow compared to pelletized ZSM-5 catalyst, structured catalysts reduce the problem of pressure drop which is responsible for the coupling of intrinsic reactions which causes more aromatics.

2.2.4 Important Applications of Zeolites

There are many important applications of zeolites catalysts in industrial processes. Some important processes which include zeolites are fluid catalytic cracking (FCC) of heavy petroleum distillates, agriculture, ion exchange processes. Table 2.1 shows some important applications of zeolites in industries.

Table 2.1 Industrial applications of zeolite catalysts [38].

Zeolite	Catalytic Process
MFI (ZSM-5,TS-1,Silicalite)	Fluid catalytic cracking, Dewaxing(cracking), MTG/MTO/MTP gasoline/olefins, Olefin cracking and oligomerization, Benzene alkylation, Xylene isomerization, Toluene disproportionation and alkylation, Aromatization, NOx reduction, Ammoxidation, Beckman rearrangement
FAU (Y)	Fluid catalytic cracking, Hydrocracking, Aromatic alkylation and trans alkylation, Olefin/paraffin alkylation, NOx reduction, Acylation
BEA (Beta)	Benzene alkylation, Acylation, Baeyer-Villiger reaction
MOR (Mordenite)	Light alkanes hydro isomerization, Dewaxing(cracking), Aromatic alkylation and trans alkylation, Olefin oligomerization
LTL (KL)	Alkane aromatization
MTW (ZSM-12)	Aromatic alkylation
MWW(MCM-22)	Benzene alkylation
FER (Ferrierite)	n-Butene skeletal isomerization
TON (Theta-1, ZSM-22)	Dewaxing (long chain alkane hydro isomerization), Olefin skeletal isomerization
AEL (SAPO-11)	Dewaxing (long chain alkane hydro isomerization)
ERI (Erionite)	Selective forming
CHA (SAPO-34)	MTO

2.3 Conversion of Methanol to Propylene

Methanol is converted to propylene using zeolite ZSM-5 catalyst. Methanol itself can be produced from synthesis gas, coal and biomass [39]–[41]. Synthesis gas is the most important feedstock for the production of methanol in industries worldwide. Synthesis gas has been produced by using natural gas by steam reforming process. MTP process is mainly conducted in a fixed bed reactor system developed by Lurgi over ZSM-5 catalyst for propylene optimization. MTP process is an easy process of methanol conversion to propylene, it's a low-pressure operation mainly conducted at atmospheric pressure. The typical process variables are temperature, pressure and weight hourly space velocity (WHSV). Selectivity of propylene in MTP is optimized by using these parameters during the reaction and recycling other HC's as well [13]. Apart from propylene, ethylene and other olefins and gasoline are the main products depending on reaction conditions.

A schematic diagram of Lurgi MTP process has been shown in Figure 2.8. In this

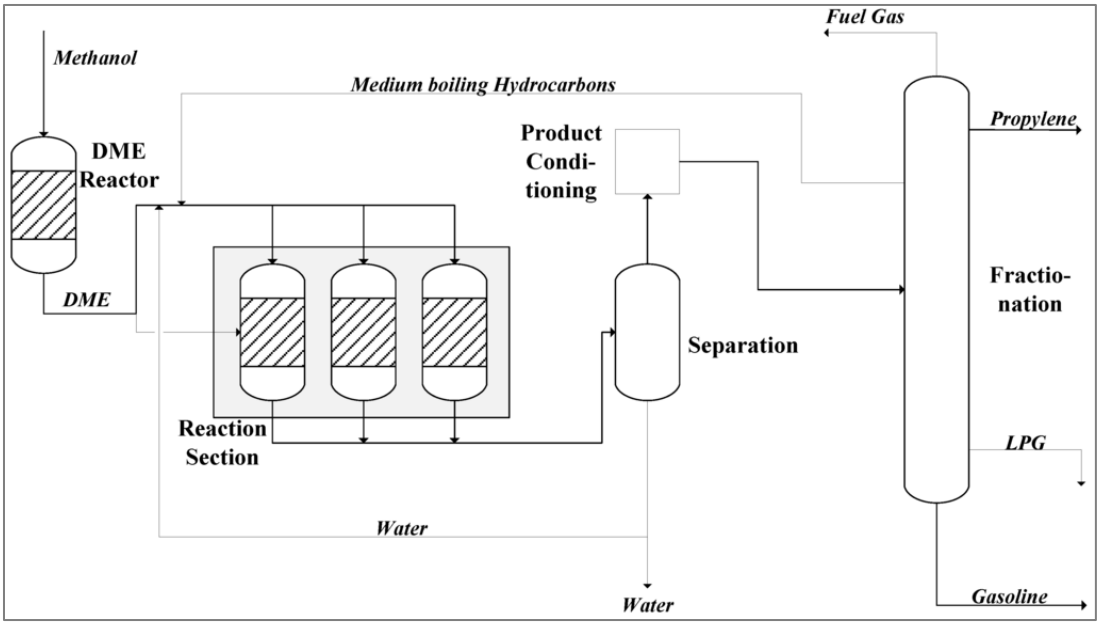


Figure 2.8 Lurgi's methanol to propylene process[43].

process first, methanol converts to dimethyl ether and steam at high temperature. Dimethyl ether than reacts over ZSM-5 to produce various HC gasses. The resulting effluents are cooled and separated in a sequence. In purification section, propylene and gasoline are separated. The advantage of this process is that it produces polymer grade propylene, zeolite catalyst regeneration, and simple fixed bed reactor system. The production plant consists of three parallel reactors which enable intermittent regeneration [42].

In china ethylene and propylene was traditionally produced from either steam cracking or catalytic cracking. MTO and MTP processes provide alternative routes for the production of highly demanding olefins. China has a high ratio of polymer per person consumption. In the present time china mainly using two technologies i.e. Lurgi MTP process and DMTO process to fulfill its olefins demand mainly propylene. Low-cost methanol availability in china has brought Lurgi MTP process commercially. The first commercial MTP plant in china was started in 2010 with 500000 tons annually [42]. By using ZSM-5 catalyst Lurgi process claims around 70% propylene selectivity from dimethyl ether. Based on Lurgi process a plant has been in operation in Iran with almost 100000 tons yield of olefins and is a major contributor to meet the olefins requirement of the country [5].

2.4 Modification of ZSM-5 Catalyst towards Propylene Selectivity

Increase in olefins demand forced researchers to modify zeolite catalysts by using metals and semi-metals or by improving the surface area so that more catalytic reactions can be possible on the zeolite surface.

2.4.1 Modification by Metals loading

The ZSM-5 zeolite contains special three-dimensional channels, which can obstruct the formation of large HC's, thus inhibiting coke deposition and improving the catalytic stability. Modification of ZSM-5 can increase the light olefin selectivity and the catalytic stability [11], [44], [45]. Modification by metals results in acidity adjustment of the zeolites. Increasing the SiO_2/Al_2O_3 ratio in ZSM-5 can enhance the selectivity of light olefins in the methanol conversion over the zeolite catalysts with different SiO_2/Al_2O_3 ratios [46], [47]. At present, the ZSM-5 zeolite is widely applied in such reactions as alkane dehydrogenation, aromatization, catalytic cracking. The structure of ZSM-5 zeolite is not destroyed by the introduction of metal components.

For a supported multi-component catalyst prepared by impregnation, the method for preparation of the catalyst, especially the impregnation sequence of the metal precursor, is known to be an important factor for the performance of catalysts ZSM-5 zeolites. They are also modified by impregnation with various metallic salts, thereby increasing the selectivity to light olefin due to a decrease in the apparent pore size. During the process of catalyst synthesis, various metal salts are added at the stage of gel formation to modify the ZSM-5 zeolite by the rapid crystallization method. Impregnation of metals like Fe, Ce, W, Co and Pt exhibit the best selectivity to light olefins [48], [49]. Figure 2.9 reflects the effect of metals and semi-metals loading on zeolite ZSM-5 (SiO_2/Al_2O_3=200) [44].

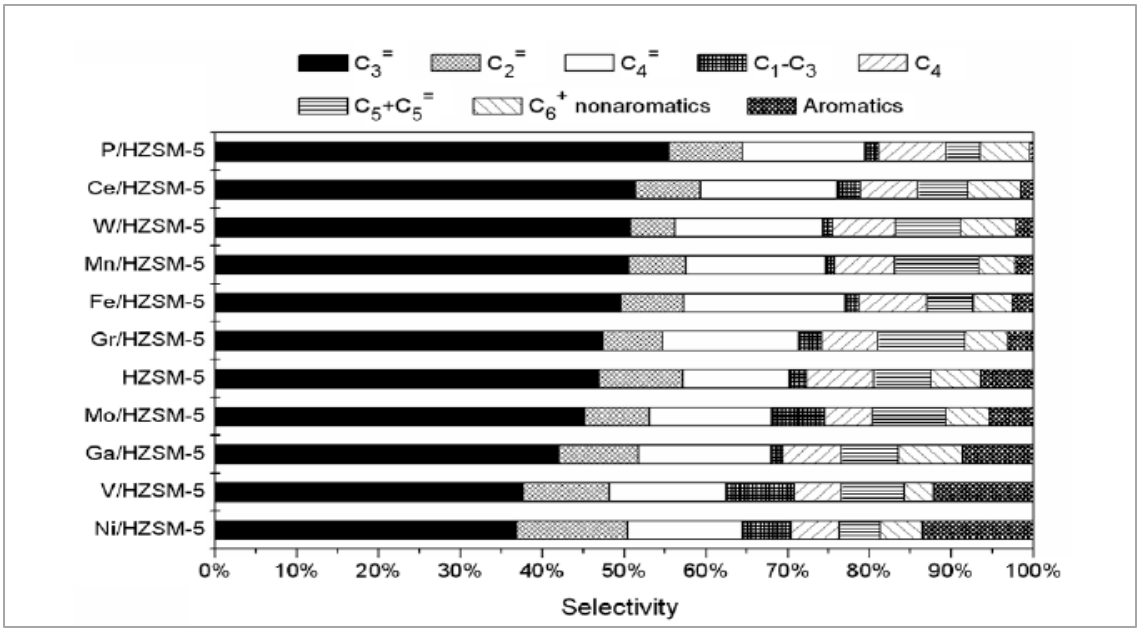


Figure 2.9 ZSM-5 (200) modification by metals and semi-metals.

In the recent year's high propylene selectivity has been reported in papers by incorporating boron, phosphorus, iron, nickel, iridium, manganese on the parent zeolite catalysts [45], [48]–[50], [37], [51], [52]. Jiao [37] in his study of MTO reported 21% increase in propylene selectivity by Fe loading on ZSM-5 (SiO_2/Al_2O_3=100) due to decrease in the strong acid sites. Suhong [53] reported 50% propylene selectivity by calcium modification on ZSM-5 (106), Hadi [54] reported 45% propylene selectivity using Mn/ZSM-5 (200) catalyst, Yisu Yang [55] reported 47% propylene selectivity using bimetallic B-Al/ZSM-5 (200) catalyst, high propylene selectivity about 55% is reported by Jian Liu [12] by phosphorus-modified ZSM-5 (220) catalyst. This all improvements by metals and semi-metals loadings are due to the partial elimination of strong acid sites due to which there is a balance between weak and strong acid sites in modified ZSM-5 catalyst. Nickel modification on SAPO-34 catalyst improves ethylene selectivity due to improved framework structure [56].

2.4.2 Modification of Zeolite by Phosphorus

The best way of improving the performance of zeolite ZSM-5 catalyst for the propylene selectivity is by introducing phosphorus in MFI structure. The introduction of phosphorus in ZSM-5 catalyst decreases the acidity and hence reduces aromatics formation in MTP [44], [57]–[60]. Phosphorus has been used for ZSM-5 modification in the processes fluid catalytic cracking, MTH and toluene alkylation [61]. Phosphorus not only improves propylene selectivity but also improves the hydrothermal stability of zeolite ZSM-5 catalyst [62]–[66]. The stability of the catalyst is very important by the introduction of any promoters because water is present in MTP reaction and it causes dealumination and hence deactivation of catalysts. Figure 2.10 shows some models summarized by Lercher on how phosphorus interact with the ZSM-5 catalyst.

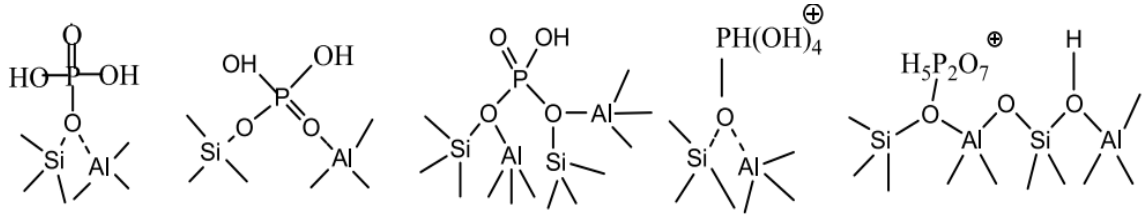


Figure 2.10 Different model on ZSM-5 and phosphorus interaction [61].

The mechanism on how phosphorus interacts during MTP reaction is controversial. Many mechanisms are proposed such as there is a connection of ZSM-5 framework and phosphorus, no framework interaction but the formation of tetrahydroxyphosphonium ions which improves catalyst performance [61], [62], [66]–[71].

2.5 Structured Catalyst

In recent years structured catalysts have been used in MTP process due to many advantages. Hydrothermally and mechanically stable structured catalysts are developed and introduced in the reactor system to improve the results in MTP reaction. Structured catalysts are developed from many structured supports including solid foams, ceramic and metallic monolith. The washcoat containing active sites is coated on these supports. Structured catalysts have crucial advantages over packed bed reactors which include better mass and heat transfer, low-pressure drop and contact time due to shorter diffusion distance and faster intra-diffusion rate of both reactants and products. Structured catalyst reactors make possible to overcome the disadvantages of traditional packed bed reactors. High propylene selectivity and less energy consumption are the key factors for replacing traditional reactors with structured catalyst reactors. Physical, chemical and geometrical properties of the structured supports are considered in making structured catalysts. High surface area of channels and microporous nature of structured support are important characteristics while making structured catalysts.

2.5.1 Monolith Support

Ceramic monolith, ceramic foam and metallic monolith supports are typically used in the preparation of structured catalysts. These three supports are shown in Figure 2.11 [72], [73]. Honeycomb monoliths are widely used structured catalysts having large industrial applications i.e. automotive catalytic converters, industrial catalytic reactors, biochemical reactors and catalytic combustion reactors.

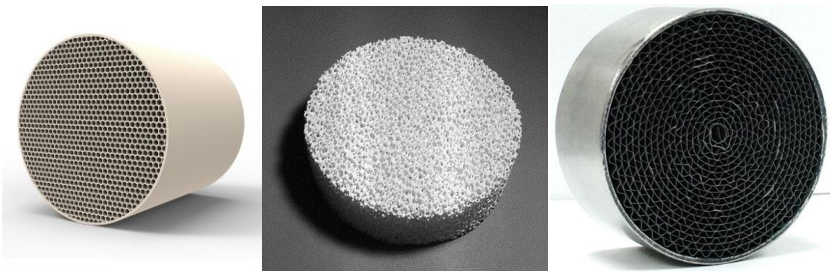


Figure 2.11 (a) Ceramic monolith support (b) ceramic foam support (c) metallic monolith support.

Monolith supports are either ceramic or metallic in nature. Both of these supports have advantages and disadvantages. The selection of these supports depends on the process conditions and end applications. Normally metallic monoliths have thin walls compared to ceramic monolith supports. The thin wall thickness of metallic monolith supports enables the structure to have short warm-up time which results in better efficiency. Ceramic monolith supports are cheaper in cost than metallic monolith supports.

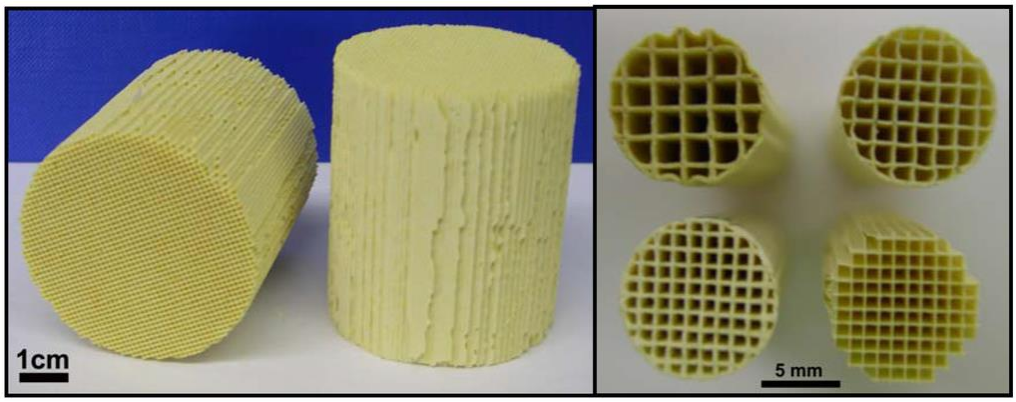


Figure 2.12 Honeycomb monolith supports [76].

Ceramic monoliths have macroporous wall which allow the catalysts to disperse finely on the monolith wall which results in a fine washcoat [74], [75]. A honeycomb monolith support can be characterized on the basis of cell density, shape wall thickness. Ceramic

monoliths are mainly made from cordierite (14 wt% MgO, 36 wt% Al_2O_3 and 50 wt% SiO_2) [19]. Figure 2.12 shows honeycomb ceramic monolith support with different cell densities.

2.5.2 Monolith Structured Catalysts in MTP

Due to many advantages of structured catalyst over powder catalyst, these catalysts are employed in MTP process. A high hierarchical porous catalyst can be obtained by microporous zeolite coating on macroporous monolith support. Monolith structured catalysts can be prepared by washcoating or hydrothermal coating or combination of both. High cell density and the thinner wall of structured catalyst exhibits maximum conversion and propylene selectivity in MTP [17]. Monolith reactor is most widely used structured catalytic system [18]. Powdered catalysts in packed bed reactor system can have a problem of plugging. Monolith catalyst reactors provide higher reaction rate with better heat and mass interactions. Appropriate selection of monolith support is necessary to overcome the problem of interconnectivity among channels and poor heat conductivity. Monolith with 400 cells per square inch (CPSI) is considered best in MTP reaction [77]. Lefevere and Gysen [78] reported high methanol conversion 100% with C_2-C_3 selectivity 41% using honeycomb monolith structured catalyst and C_2-C_3 selectivity 66% with 88% methanol conversion using ZSM-5 (25) coated stainless steel 3DFD at a high space velocity of 18 h^{-1} at 350 °C. Patcas [79] studied the effect of ceramic foams in methanol to olefins conversion and reported the substantial activity and selectivity of olefins as compared to zeolite pellets. Figure 2.13 compares packed bed pelletized catalyst and monolith structured catalyst in the fixed bed reactor system.

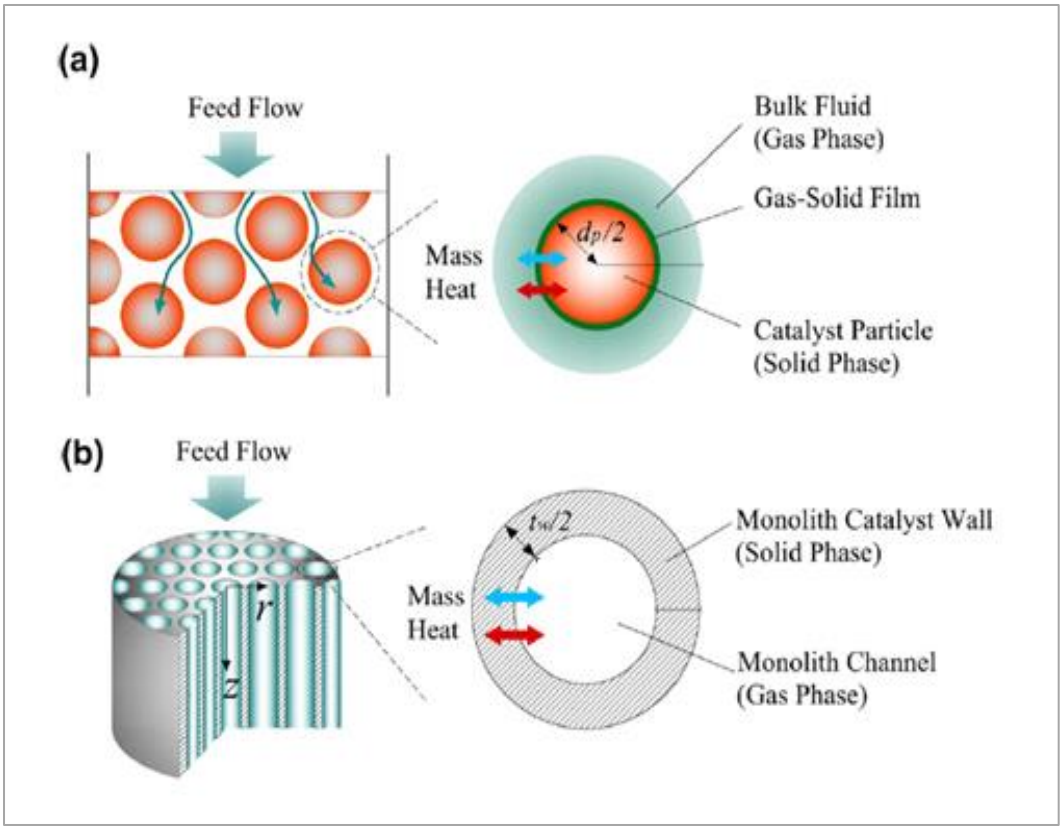


Figure 2.13 (a) Catalyst bed in fixed bed reactor system zoom on one pellet, (b) Monolith catalyst zoom on single monolith channel [77].

2.5.3 Methods of Zeolite Coating on Monolith

The zeolite coating on monolith support can be done either by wash coating or by a hydrothermal coating method or a combination of both. Wash coating by dip coating method is an easy way of zeolite coating active on monolith support. In this method, a slurry having a catalyst with the binder is prepared. Wash coat quality depends on the monolith wall solid phase and the prepared slurry. An alternative to dip coating is spray coating, spray coating on high cells monolith structure is very difficult. Wash coat quality also depends on the amount of catalyst in the slurry and calcination temperature [80]. Microporous catalyst on macroporous monolith support resists the formation of the pinhole on the monolith wall and

coating usually is uniform. Binder plays an important role in the preparation of slurry as it defines the amount of zeolite coating on the monolith. Though binder has some adverse effect on the performance of catalyst as it affects the amount of acidity or active sites of the catalyst. In dip coating method monolith support is dipped into the slurry for some time then removed from it. Pressurized air is passed through the monolith channels to avoid any excess slurry. The Higher amount of zeolite loading on cordierite monolith support can be achieved with multilayer coating by repeating coating for one, two or three times. Apart from this, a coating of zeolite on monolith can be done by in situ method. In this method, monolith support is simply dipped in the zeolite synthesis gel during catalyst preparation. Under the right conditions of zeolite synthesis, the crystals grow on the surface of monolith support [81].

2.6 Reaction Mechanism in MTP

Reaction mechanism in MTP is always controversial. Extremely complex reaction network makes it difficult to explain the mechanism of MTP process. Zeolites are highly porous materials and attention should be focused on the diffusion and desorption of reactant and products inside the pores [25]. There are many steps involve in methanol conversion to hydrocarbons, the general equation can be written as:

$$\frac{n}{2}[2CH_3OH \rightarrow CH_3OCH_3 + H_2O] \xrightarrow{-nH_2O} C_nH_{2n} \rightarrow n[CH_2] \quad (2.1)$$

Methanol Dimethyl Ether Water Olefins Paraffins + Aromatics

In the first step, methanol dehydrated to DME and water. DME, water and methanol mixture produce light olefins in the subsequent step. In the last step, light olefins are

converted to higher olefins, paraffins and aromatics by hydrogen transfer, cyclization and oligomerization reactions. Formation of DME can be explained as methanol molecule reacts with OH group on the active sites to form a surface methoxyl, which is then attacked by another methanol molecule [10].

Early proposals for methanol conversion to olefins deal with direct coupling of C-C bond. Dessau [82] proposed the alkene methylation or cracking mechanism for the MTH reaction shown in Figure 2.14. According to his proposal, methanol is converted to hydrocarbons through repetitive methylation of light olefins to form higher olefins which undergo further methylation or cracking reactions. In addition, aromatic species formed during the MTH reaction only exist as end products resulting from hydrogen transfer reactions.

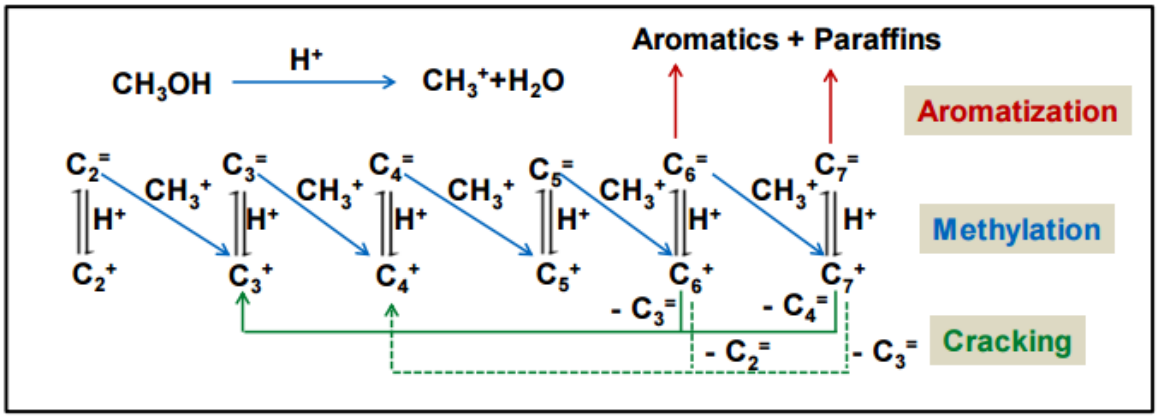


Figure 2.14 An olefin homologation/cracking mechanism proposed by Dessau.

2.6.1 Hydrocarbon Pool Mechanism

Dahl and Kolboe proposed a 'hydrocarbon pool mechanism', according to this mechanism methanol forms a pool of $(CH_2)_n$ species within the pores of the zeolite that

produces light olefins, alkanes and aromatics [83]–[85]. According to hydrocarbon pool, in MTP reaction the active center is an organic species adsorbed on the surface of zeolite pores and cages. Dahl and Kolboe establish the role of aromatics, especially in conversion to light olefins formation, the aromatics are mainly methyl benzenes. In the proposed cycle methanol reacts with methyl benzenes via methylation which produces light olefins i.e. ethylene and propylene. Alkenes and arenes are thought of as intermediate species in the pool.

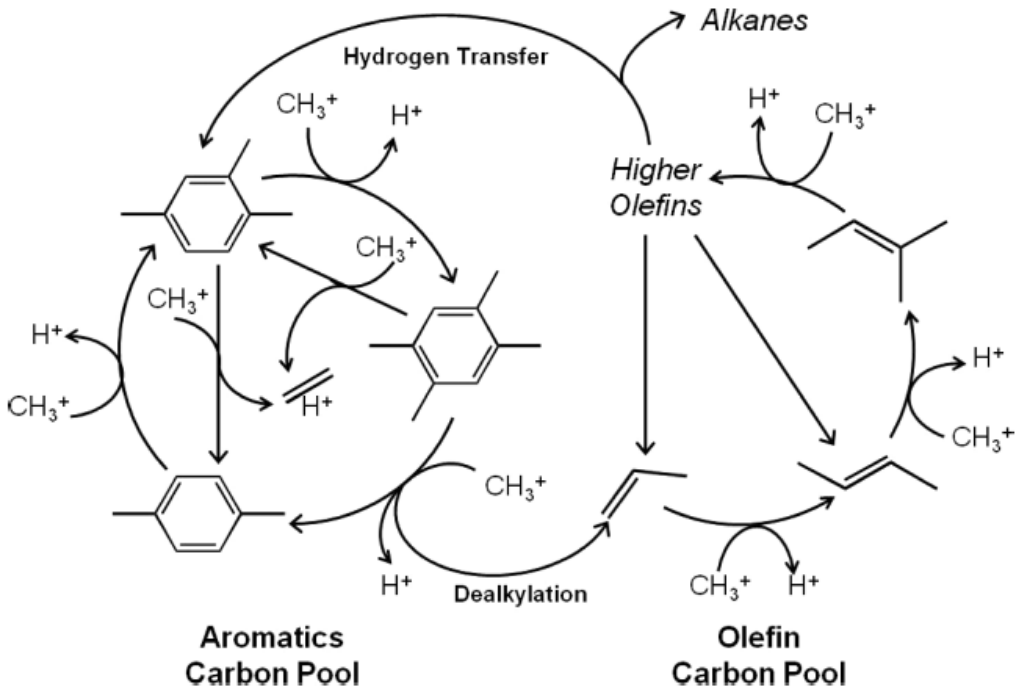


Figure 2.15 Hydrocarbon Pool Mechanism.

According to the mechanism, two HC pool cycles exist in ZSM-5 catalysts which is shown in Figure 2.15. Ethylene is predominantly formed from lower methylbenzene while propylene and higher alkenes are considered to form by the methylation and cracking reactions.

2.6.2 Typical Reactions involved in MTP Process

There are about 726 elementary steps in which 142 olefins with carbon number below 9 and 83 carbenium ions in the methanol to propylene conversion process. In MTP reaction, first methanol gets dehydrated to form olefins including butane, pentene, hexene and heptene. These higher olefins then undergo a series of methylation reactions. There is cracking of heavier components such as hexene and heptane to lighter olefins. During the cracking of higher paraffin like heptane produces lighter paraffins such as ethane, propane, butanes, pentanes and the aromatics. Methane is produced directly from methanol [86]. In this work the main objective is to increase the propylene selectivity by modifying the ZSM-5 catalyst, so the main olefin reactions considered here are [77]:

$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O$ *(considered in equilibrium)*

$CH_3OH + C_3H_6 \longrightarrow C_4H_8 + H_2O$

$CH_3OH + C_4H8 \longrightarrow C_5H_{10} + H_2O$

$CH_3OH + C_5H_{10} \longrightarrow C_6H_{12} + H_2O$

$CH_3OH + C_6H_{12} \longrightarrow C_7H_{14} + H_2O$

$C_7H_{14} \rightleftharpoons C_3H_6 + C_4H_8$

$C_6H_{12} \rightleftharpoons 2C_3H_6$

$C_6H_{12} \rightleftharpoons C_2H_4 + C_4H_8$

$2C_5H_{10} \rightleftharpoons C_3H_6 + C_5H_{10}$

$2C_4H_8 \rightleftharpoons C_3H_6 + C_5H_{10}$

$C_7H_{14} \longrightarrow C_7H_8 + 3H_2$

$2C_4H_8 \longrightarrow C_8H_{10} + 3H_2$

$$2C_8H_{10} \rightleftharpoons C_7H_8 + C_9H_{12}$$

$$C_9H_{12} + H_2 \rightleftharpoons C_8H_{10} + CH_4$$

$$C_2H_4 + H_2 \rightleftharpoons C_2H_6$$

$$C_3H_6 + H_2 \rightleftharpoons C_3H_8$$

$$C_4H_8 + H_2 \rightleftharpoons C_4H_{10}$$

CHAPTER 3

EXPERIMENTAL

This chapter highlights experimental setup and procedures involved in carrying out this research work. It gives an overview of catalyst preparation, reactor preparation, catalysts testing and characterization methods involved. Experimental was planned as catalyst preparation, installation of experimental setup with online GC, Carrying base experiments for suitable catalyst and operating reaction conditions, modification of zeolite by using metals and semi-metals impregnation, coating of zeolite on monolith support and finally characterizations for surface area, phase detection, acidity and surface morphology of best catalysts.

3.1 Catalyst Preparation

Catalyst preparation is a critical part in any research. The end products in MTP process depends typically on acidity, porosity and crystal size of the zeolite catalyst, therefore it's important to control and synthesize a suitable zeolite catalyst which can improve propylene selectivity in MTP process. In this study HZSM-5, FeHZSM-5, modified HZSM-5, Monolith coated HZSM-5 and Monolith coated P impregnated HZSM-5 catalysts were prepared and evaluated in the fixed bed reactor system.

3.1.1 Chemicals Used

The chemicals used in catalyst preparation were purchased from Sigma-Aldrich. Chemicals that were used are TEOS (tetraethyl orthosilicate, >99.0 %), TPAOH (tetra propyl ammonium hydroxide, 1.0 M in water), NaOH (sodium hydroxide, 5.0M in water), H_2SO_4 (sulphuric acid, 1% in water), Fe $(NO_3)_3.9H_2O$ (iron (iii) nitrate nona hydrate, >99.0%), H_3PO_4 (orthophosphoric acid, 65%), Ce $(NO_3)_3.6H_2O$ (cerium (iii) nitrate hexa hydrate, >99.0%), La $(NO_3)_3.H_2O$ (lanthanum (iii) nitrate hydrate, >99.0%).

3.1.2 HZSM-5 Catalysts Preparation

NH_3-ZSM-5 catalysts with SiO_2/Al_2O_3 molar ratio of 30, 50, 80, 280 and 410 were procured from ZEOLYST International. These zeolites were calcined at 550 °C for 6 hours to obtain in H-form and to remove any impurities.

3.1.3 Metal Modified HZSM-5 Catalysts Preparation

Incipient impregnation technique was used for the modification of catalysts. Incipient impregnation by pore filling method is a simple method in which metal precursor was poured on the catalyst sample. For impregnation, all catalyst were calcined at 550 °C for 3 hours and kept into desiccator to avoid moisture. The incipient pore volume of the required solution for impregnation was calculated based on 1 gm of the catalyst by adding dropwise DI water and this amount of water was used for making metals and semi-metal promoters solution. Promotor solution with required amount of loading was prepared and this solution was added to the powdered catalyst, all impregnated samples were dried

overnight at 110 °C and calcined at 450 °C for 6 hrs. Prior to testing on fixed bed reactor system all samples were pelletized, crushed and sieved to 0.5-1 mm size. Figure 3.1 shows the metal loading procedure by incipient impregnation technique.

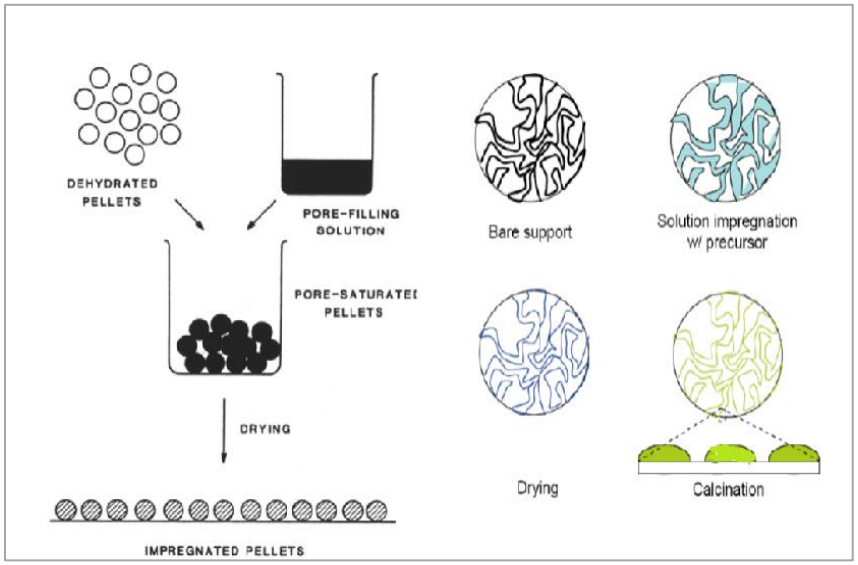


Figure 3.1 Impregnation of zeolite catalysts by pore filling method.

3.1.4 FeHZSM-5 Catalysts Preparation Method

Three zeolite samples with SiO_2/Fe_2O_3 molar ratio of 80, 100 and 150 were prepared using steps discussed in the literature [87]. TPAOH (12 gm for ratio 80) and (15gm for ratio 100 and 150) was taken into a beaker. The solution was kept on a magnetic hot plate and stirred at 800 rpm. $Fe(NO_3)_3.9H_2O$ (0.4015 gm for ratio 80) and (0.30 gm for ratio 150) was added dropwise to the TPAOH solution and stirred for 30 minutes to obtain homogenous mixture. The desired amount of TEOS was added dropwise to this solution and stirred for next 1 hour at room temperature. This solution was then stirred for 3 hours at 100 °C to completely hydrolyze TEOS, after this the mixture was further stirred at 800 rpm for next 20 hours at room temperature. The pH was checked and maintained about 11 by adding

either NaOH or H_2SO_4. The mixture was then transformed into a Teflon-lined autoclave and was put into the furnace for 48 hours at 180 °C with 2 °C/min ramp rate. The sample obtained was washed several times in DI water and acetone with centrifuge at 900 rpm to remove the template. Ion-exchange was carried out in 0.1 M NH_4NO_3 solution then was centrifuge again in a similar way. After this the sample was dried in an oven at 110 °C overnight then calcined at 550 °C for 6 hours to get final catalyst in FeHZSM-5 form.

Table 3.1 shows all apparatus used in catalyst preparation/modifications during the study. Table 3.2 reflects the physical and thermodynamic properties of pure methanol.

Table 3.1 Apparatus used in catalyst preparation.

Apparatus	**Model or Specification**	**Manufacturer**
Hot Plate with Stirrer	MSH-20D	Wise Stir
Balance	ALC-210	Acculab
pH meter	AB 15	Accumet
Oven	-	Genlab
Ultrasonic bath	DR-P60	Derui
Furnace	P330	Nabertherm

Table 3.2 Physical and thermodynamic properties of pure Methanol [96].

Molecular Weight	32.04 g mol^{-1}
Critical Temperature	512.5K (239°C; 463°F)
Critical Pressure	8.084MPa (78.5 atm)
Critical Density	0.2715 g cm^{-3}
Critical Compressibility Factor	0.224
Specific Gravity	
Liquid	
(25°/4°C)	0.7866
(20°/4°C)	0.7915
(15°/4°C)	0.7960
Vapour	1.11
Vapour Pressure	
20°C (68°F)	12.8 kPa (1.856 psia) (96 mm Hg)
25°C (77°F)	16.96 kPa (2.459 psia) (127.2 mm Hg)
Latent Heat of Vapourization	
25°C (77°F)	37.43 kJ mol^{-1} (279.0 cal g^{-1})
64.6°C (148.3°F)	35.21 kJ mol^{-1} (262.5 cal g^{-1})
Heat Capacity at Constant Pressure	
25°C (77°F) (101.3kPa)	
Liquid	81.08 J mol^{-1} K^{-1} (0.604 cal g^{-1} K^{-1}) (0.604 Btu lb^{-1} $°F^{-1}$)
Vapour	44.06 J mol^{-1} K^{-1} [1] (0.328 cal g^{-1} K^{-1}) (0.328 Btu lb^{-1} $°F^{-1}$)
Coefficient of Cubic Thermal Expansion	
20°C	0.00149 per °C
40°C	0.00159 per °C

Boiling Point	
760 mm Hg (101.3 kPa)	64.6°C (148.3°F)
Freezing Point	-97.6°C (-143.7°F)
Reid Vapour Pressure	32 kPa
Flash Point	
Closed vessel (TCC method)	12°C (54°F)
Open vessel (TOC method)	15.6°C (60.1°F)
Auto Ignition Temperature	470°C (878°F)
Viscosity	
Liquid	
-25°C (-13°F)	1.258 mPa s
0°C (32°F)	0.793 mPa s
25°C (77°F)	0.544 mPa s
Vapour	
25°C (77°F)	9.68 µPa s
127°C (261°F)	13.2 µPa s
Surface Tension	
20°C (68°F)	22.6 mN m^{-1}
25°C (77°F)	22.07 mN m^{-1}
Refractive Index	
15°C (59°F)	1.33066
20°C (68°F)	1.32840
25°C (77°F)	1.32652
Thermal Conductivity	
Liquid	
0°C (32°F)	207 mW m^{-1} K^{-1}
25°C (77°F)	200. mW m^{-1} K^{-1}
Vapour	
100°C (212°F)	14.07 mW m^{-1} K^{-1}
127°C (261°F)	26.2 mW m^{-1} K^{-1}
Heat of Combustion	
Higher heating value (HHV) (25°C, 101.325kPa)	726.1 kJ mol^{-1} (22.7 kJ g^{-1})
Lower heating value (LHV) (25°C, 101.325kPa)	638.1 kJ mol^{-1} [calc] (19.9 kJ g^{-1})
Flammable Limits (in air)	Lower 6.0(v/v)% Upper 36.5(v/v)%

3.1.5 Monolith Structured Zeolite Catalysts Preparation

The zeolite coating on a structured support can be done by either wash coating or hydrothermal coating or a combination of both [88]–[93]. The structured catalyst was prepared by dip coating method which falls in washcoating technique on cordierite monolith

support. Honeycomb cordierite monolith structured support with 400 CPSI was used for zeolite coating in the study. Dip coating was done in three steps, in the first step cordierite monolith support was washed in 5 wt% HNO_3 DI water solution for 20 minutes then dried at 110 °C for 6 hours followed by calcination at 550 ˚C for 6 hours. In the second step, a slurry having 20 wt% ZSM-5 zeolite with 1 wt% colloidal silica (Ludox AS-40) in 20 grams of DI water was prepared. The slurry was stirred for 6 hours on a magnetic stirrer at 600 rpm at ambient temperature then treated in an ultrasonic bath for 15 mins. In the final third step, the monolith was dipped in the prepared slurry for 3 minutes, later it is removed from the slurry. A dry air was passed through the monolith channels to remove excess slurry. Zeolite coated monolith then dried at 110 °C with a ramp rate 2 °C/min in rotating oven for 12 hours followed by calcination at 500 °C with ramp rate 3 °C/min for 4 hours.

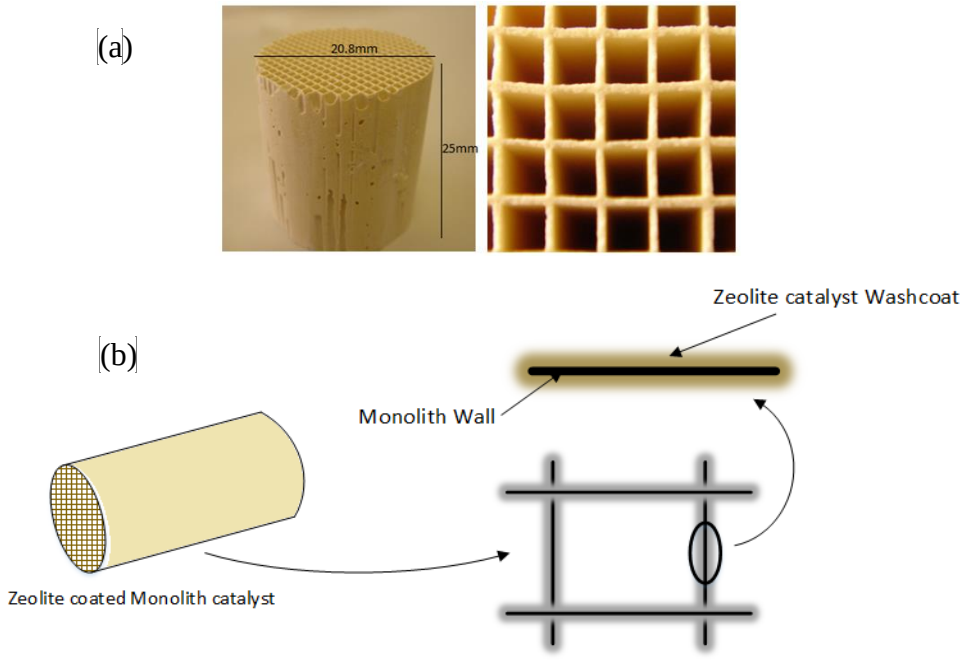


Figure 3.2 (a) Front and top view of prepared monolith catalyst (b) Enlarged view of zeolite-coated monolith channel wall.

Prepared structured catalyst was treated in an ultrasonic bath for 1 minute, thus resulting in weight loss by ultrasonic treatment provide adhesion strength of structured catalyst [94], [95]. The amount of catalyst coating adhesion was obtained from monolith coated zeolite samples. To increase zeolite coating, monolith was dipped two to three times in the left catalyst slurry. Figure 3.2 shows prepared zeolite coated structured monolith catalyst, (a) front and top view while (b) represents the enlarged view of a monolith channel wall with catalyst washcoat and Figure 3.3 shows the steps involved in modified and monolith catalyst preparation. Prepared monolith structured catalyst performance was evaluated in the fixed bed reactor system.

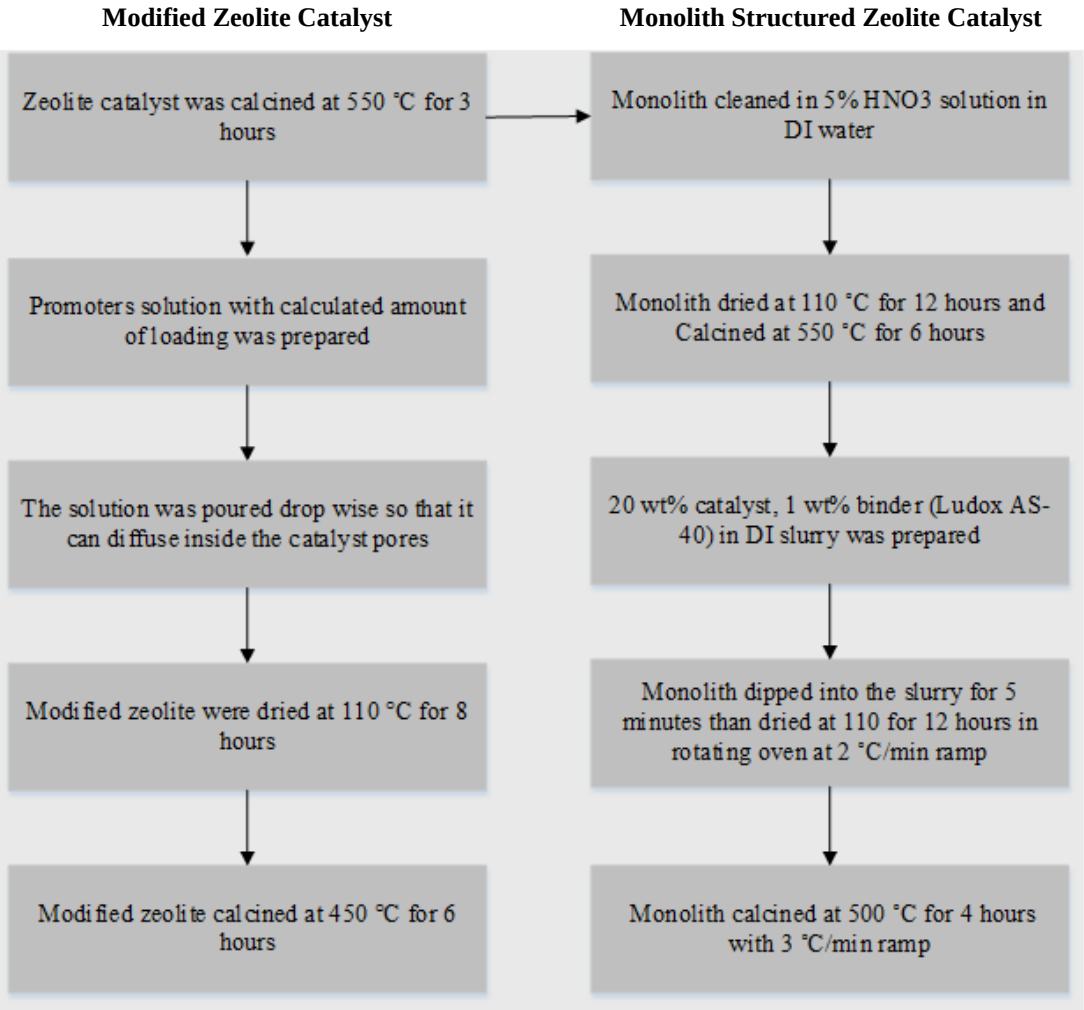


Figure 3.3 Steps involve in preparation of modified and monolith structured catalysts.

3.2 Experimental SetUp

The process diagram of the fixed bed reactor setup is shown in Figure 3. 4 while Figure 3.5 is the image of the experimental setup. The experimental setup has four sections (i) feed section, (ii) preheater, (iii) reactor section and (iv) product collection and separation section. Catalyst evaluation method is described in section 3.3 of this chapter.

3.2.1 Feed Section

The feed section of the reactor was designed to supply feed during the reaction under controlled pressure and flow rate. The feed section of the bench-scale plant consist of methanol storage tank, methanol feed pump, Inert (nitrogen) cylinder. The feed tank was filled about one-third with feed methanol. Feed tank was connected to HPLC series 1 pump. The pump was operated between flow rates of 0.10 to 0.64 ml/min. Nitrogen flow was supplied during the reaction with pressure set point 5 bar. Nitrogen gas supply was started when the temperature of the reactor reaches 300 °C. This helps in the pretreatment of catalyst in removing the presence of any impurity that entraps inside the pores.

Table 3.3 shows the design parameters of the experimental setup.

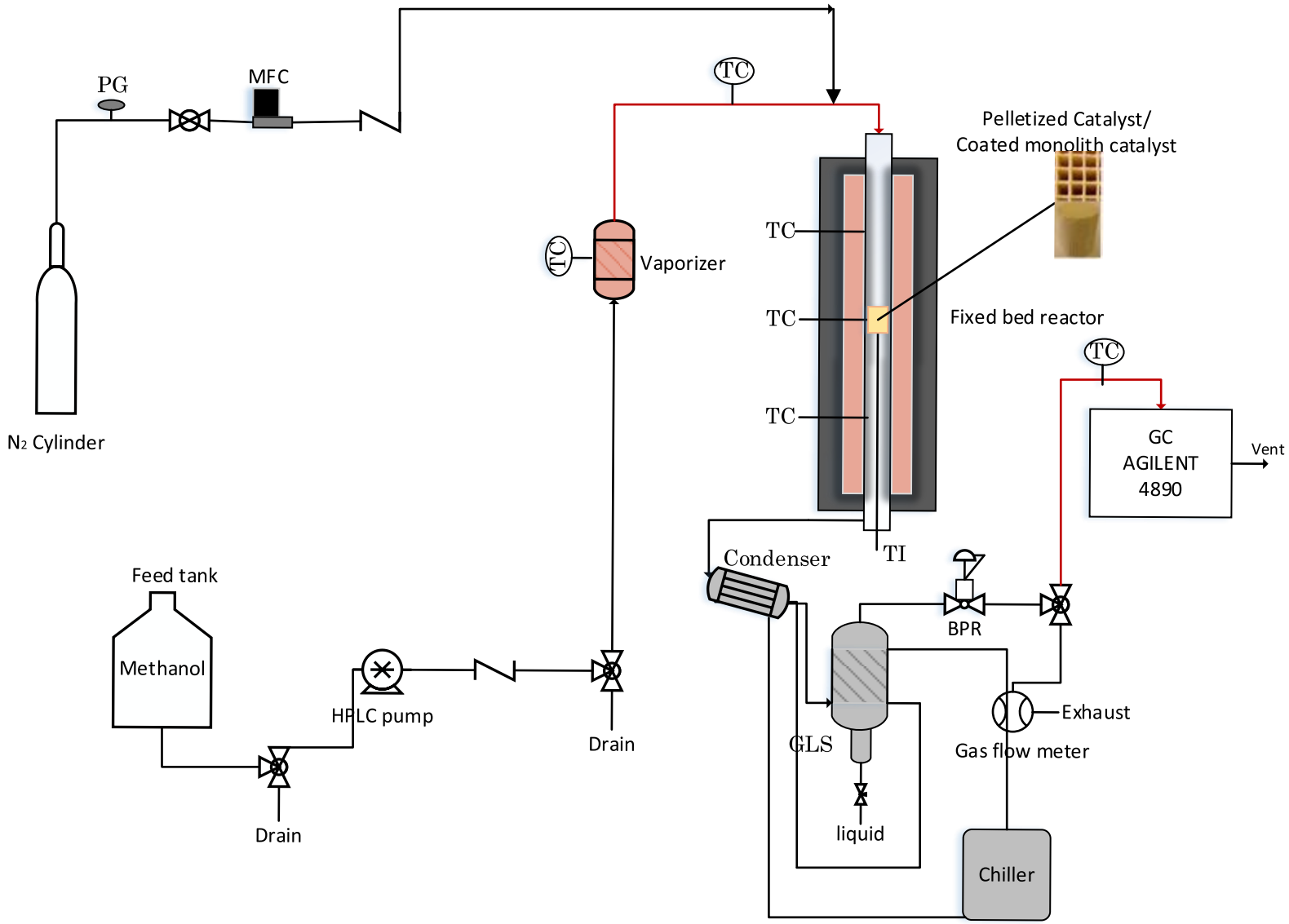


Figure 3. 4 Fixed bed reactor system

Figure 3.5 Fixed bed reactor system.

Table 3.3 Design parameters of Reaction Setup.

Parameters	Design basis
Methanol Feed rate	1 – 10 ml/min
Nitrogen flow rate	0 – 99 ml/min
Preheating temperature	200 °C
Furnace temperature	Up to 600 °C
Pressure	1 – 20 bar
Chiller temperature	Up to 5 °C

3.2.2 Preheating zone

The methanol fed by HPLC pump was preheated in the preheater whose temperature was set to 100 °C during all experiments. Heat insulation was provided from preheater to the furnace. Methanol and Nitrogen were mixed in this heated inlet line before they enter into the reactor to provide a homogenous mixture of the feed. The insulation was provided to both the preheater and line heater to ensure that there is no heat loss to the surrounding and to maintain stable temperature during the operation.

3.2.3 Reactor Section

The reactor was made of stainless steel with internal diameter 21 mm and overall length 300 mm with heating length 200 mm, the catalyst sample was placed in mid-section

of the reactor so that the thermocouple inside the reactor placed exactly in the center of the catalyst bed. There was two thermocouple attached to the reactor, one indicates the wall temperature while the other goes inside from the bottom and placed exactly in the center of the reactor.

Table 3.4 Reactor and Furnace specifications.

Reactor	
Internal dia	21 mm
Overall length	300 mm
Heated length	200 mm
Design temp	600 °C
Design pressure	20 bar
M.O.C.	SS 316
Furnace	
Inner dia	26.7 mm
Overall length	250 mm
Heated length	200 mm
Design temp	600 °C
No of zones	01
Height of each zone	200

Catalyst bed formation inside the reactor was the trickiest part of catalyst loading. SiC big particle size was filled in the bottom so that it reaches just below the top of the internal thermocouple. On this quartz wool was placed and a small size SiC particles were filled, then a catalyst with SiC mixed was filled, on this, again small size SiC particles were filled and small quartz wool was placed on this. Large size SiC particles were filled on the top so that the flow of the feed can distribute uniformly inside the reactor before it reaches the catalyst bed. A furnace with maximum temperature 600 °C was heating the reactor in

the reactor section. Table 3.4 shows the specifications of the reactor and furnace in the reactor section.

3.2.4 Product Separation Section

This section of the bench-scale plant was designed to separate the product stream in liquid and gas. The section had one condenser and a gas-liquid separator column. These two were connected to the water circulating tank whose temperature was set to 5 °C. The cooled water flows through the condenser then to the GLS column. The condensed liquid was collected out from the GLS column for the liquid analysis. The gas stream was separated in GLS and is flow from the top of the column. The gas flows through the heated outlet line connected to the GC.

3.2.5 Gas Chromatography (GC)

Chromatography is used to analyze gas and liquid samples for different compositions and is an important tool for engineers. Most of the samples we analyze are a mixture of gasses or liquids. GC has made it possible so as to determine the amount of each component in a sample mixture. The gas samples to be analyzed are injected in TCD while liquids are injected at FID at the injection port which flows in the GC column. GC columns are of two types i.e. packed column and capillary column. GC is connected with a computer to generate the peaks at different retention time. The data of these peaks are used to get the compositions of the gas samples.

Agilent 7890B GC was used in the study for gas and liquid analysis, the GC was connected online for the gas samples examination. It has both TCD (thermal conductivity detector) having GASPRO column (60m X 320µm), FID (flame ionized detector) and INNOWAX column (30m X 320µm X 0.5µm). The gas samples were analyzed into TCD while liquid samples were analyzed into FID.

GC was connected with three cylinders, that are H_2, He, Air. He was the carrier base in our GC system. To start the GC at first all cylinders were opened then GC switched on, the oven temperature was set at 250 °C in our case. Once the GC started blank run was given to avoid any unnecessary peaks in the samples. We developed two methods for data analysis, first one was 'online.gas_method' to analyze gas samples and the second was 'online.liquid_method' to analyze liquid samples. For any analysis proper sample info was given before starting the run.

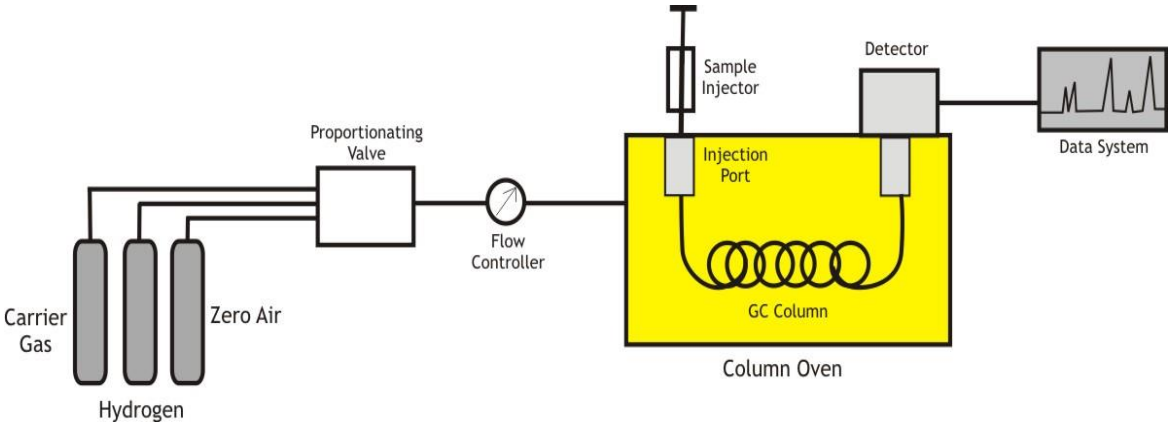


Figure 3.6 GC chromatography diagram [85].

Figure 3.6 shows schematic of GC chromatography while a typical chromatogram obtained from FID liquid analysis in the study has been shown in Figure 3.7.

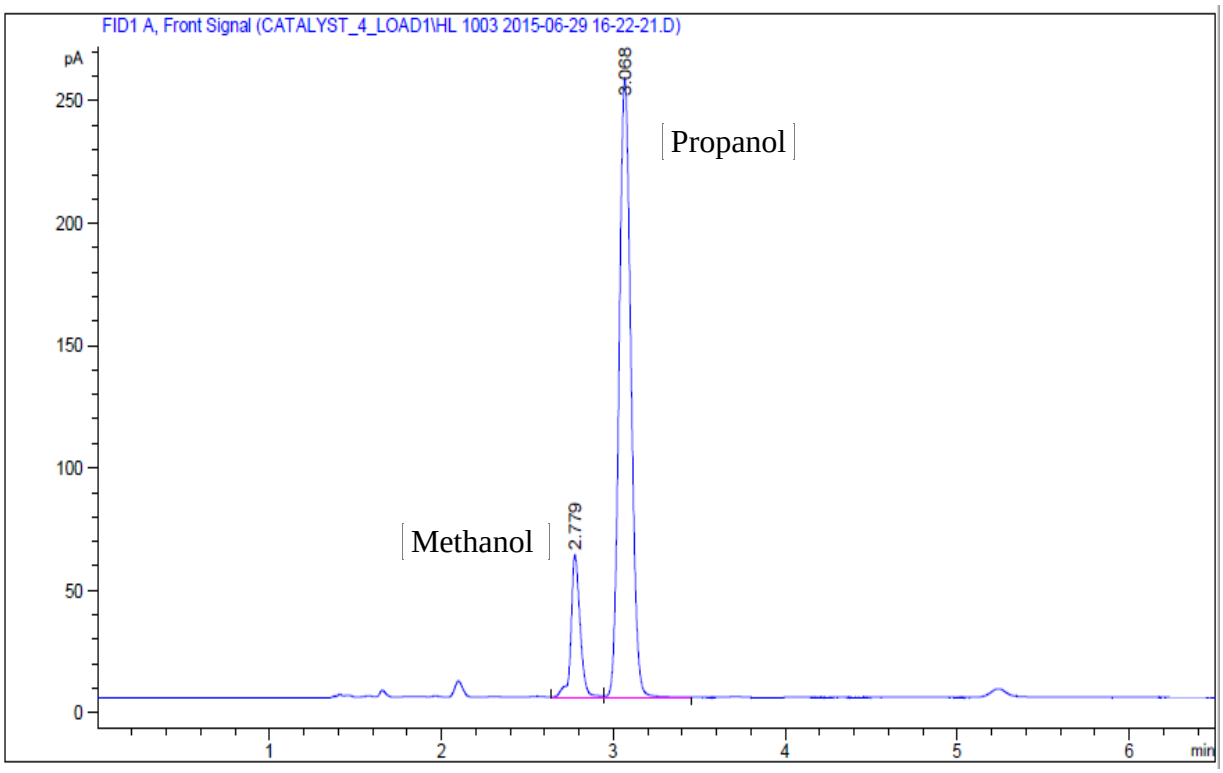


Figure 3.7 GC chromatogram obtained from FID.

3.3 Experimental Procedure

This section highlights the experimental procedure involved in the operation of the reactor which is summarized in Table 3.5. Following sections highlights the various steps involved are as follows.

3.3.1 Catalyst loading

Catalyst loading is an important step involved in the reactor operation. For each testing, 1 gm of pelletized crushed with mesh size 0.5-1 mm catalyst was loaded in the middle of the reactor shown in Figure 3.8. The bed height of the catalyst with SiC mixture was measured in a tube having the same diameter as the reactor diameter and it was 10 mm for 1gm catalyst and 4 gm SiC mixture. From the measurement obtained the catalyst bed was so formed that the top of the thermocouple fix inside the middle of the catalyst bed. SiC large particle sizes were filled in the bottom and top of the reactor to provide a proper base and to make sure that the flow of the feed was uniform.

3.3.2 Catalyst Calcination

Catalyst inside the reactor was calcined for 1 hours at 450 °C with the flow of nitrogen so that water can be purged out and any volatile substance entrap inside the pore and cavities of the catalyst can be released out, otherwise it can affect the results. The calcination involved stepwise heating which is shown in Figure 3.9. Normally the temperature was raised by the ramp rate of 5 °C/min.

Table 3.5 Experimental Procedure.

Steps	Activity
1	**Reactor Packing**
	Zeolite sample loading (1 gm)
	Pressure test
2	**Catalyst Calcination**
	Catalyst calcination at 450 °C for 1 hours
3	**Run Start**
	Reactor and preheater started and heated to set point
	Water circulating tank started
	Methanol and Nitrogen started
4	**Sampling**
	Gaseous product samples injected online into GC
	Liquid product collected and separated
5	**Run Stop and Shutdown**
	Reactor temperature given set point of room temperature
	All preheaters temperatures given set point to room temperature
	Cooler was shut down
	Reactor was shut down when its temperature fall below 50 °C

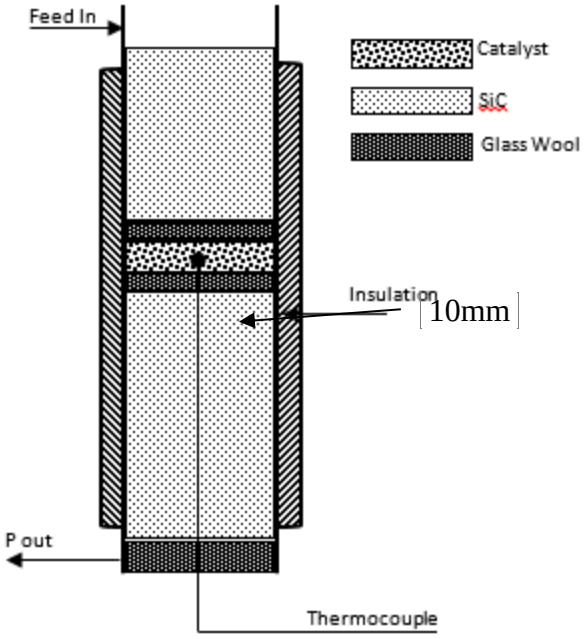


Figure 3.8 Catalyst bed formation in Reactor.

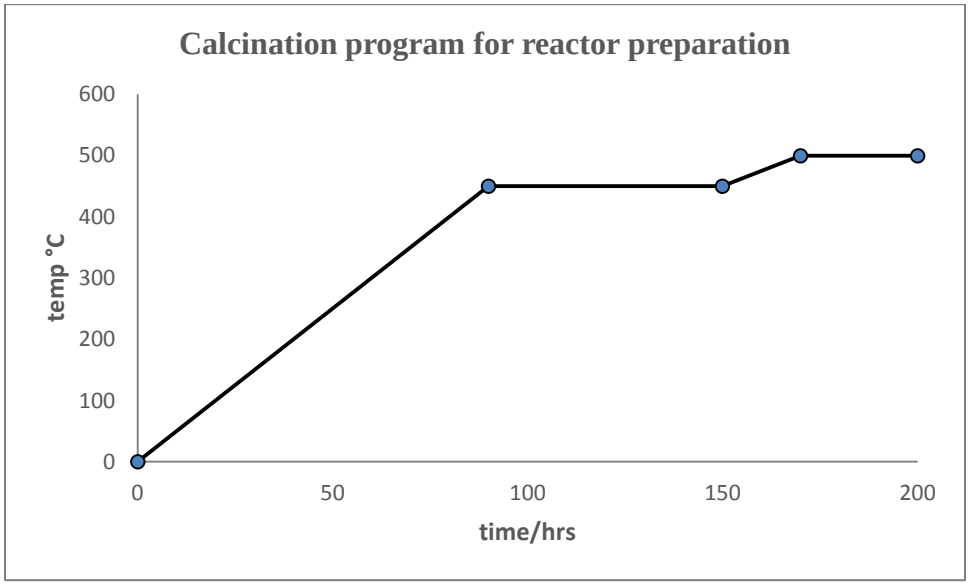


Figure 3.9 Calcination program for reactor preparation.

3.3.3 Reactor Run Start

The experimental setup units were prepared for a run by starting the various sections of the bench-scale plant. The preheaters and the coolers were started and allowed to reach the set point temperatures. Before starting the experiment, the online GC was started by opening the valves of hydrogen, air, and helium cylinders. GC was switched on and it took about 15 mins to reach 250 °C oven temperature and get ready for the analysis. Prior to the analysis always two blank runs were given to clean GC columns. Before starting pump always methanol was primed so that any air entrap in the pump line can be removed. It was also checked that all thermocouples function properly and valve positions are proper to avoid any accident. After ensuring all these things methanol feed tank was started with predetermined flow rate. Stopwatch starts immediately while starting the pump. There was a dead zone from the pump line to the reactor inlet. In this study, it was found that feed was taking 1-2 minutes to reach inside the reactor for methanol flow rate 0.24 to 0.64 ml/min. The adjustment was done accordingly. Generally, there is an increase in the temperature when the reaction starts. All parameters including temperature, pressure, flow rates were monitored carefully to avoid any interruption during the experiments. The gaseous flow rate was measured continuously during the experiment by an Agilent flow meter.

3.3.4 Sampling

Product gas analysis was done through an online GC at regular interval. The first sample was injected after 30 min time of stream and the subsequent samples were injected after an interval of 60 min, normally the time of stream was taken 2.5 hours in the study

except for the long runs in which catalyst deactivation time was studied. The liquid sample was collected at the last. The liquid sample contains aromatics, water, methanol, dimethyl ether. Aromatics was separated using a separating funnel. The heavy liquid left was analyzed in the GC by an internal standard method for liquid analysis, for unconverted methanol which gives the conversion during this time of stream.

3.3.5 Run stop and Shutdown

Once the liquid sample was collected from the GLS column the reactor was shut down by lowering its temperature to the room temperature. All preheater's temperatures were now set to room temperature. In the last liquid analysis was done for unconverted methanol analysis. After getting the final result of the liquid analysis, GC was put on standby and it took almost 45 mins to get ready for the switch off. N_2 flow was stopped when the reactor temperature get down to 300 °C. Once the reactor temperature cools down to below 50 °C, the reactor was dismantled and cleaned for the next run.

3.3.6 Liquid Analysis by Internal Standard Method

The internal standard method was used for the liquid analysis. An internal standard (propanol in this study) was added in a constant amount to all samples. Calibration involves plotting the ratio of the analyte (methanol) signal to the internal standard (propanol) signal as a function of the analyte concentration of the standard. This ratio was used to obtain the concentrations of analyte. The ratio is termed as response factor (RF):

$$RF = \frac{A_x/A_{is}}{M_x/M_{is}} \tag{3.1}$$

M_x : Mass of component unknown (methanol)

M_{is} : Mass of internal standard (propanol)

A_x : Area of component unknown (methanol)

A_{is} : Area of internal standard (propanol)

In the present study, the RF value obtained from internal standard method was 0.668 for methanol and propanol standard which is shown in Figure 3.10.

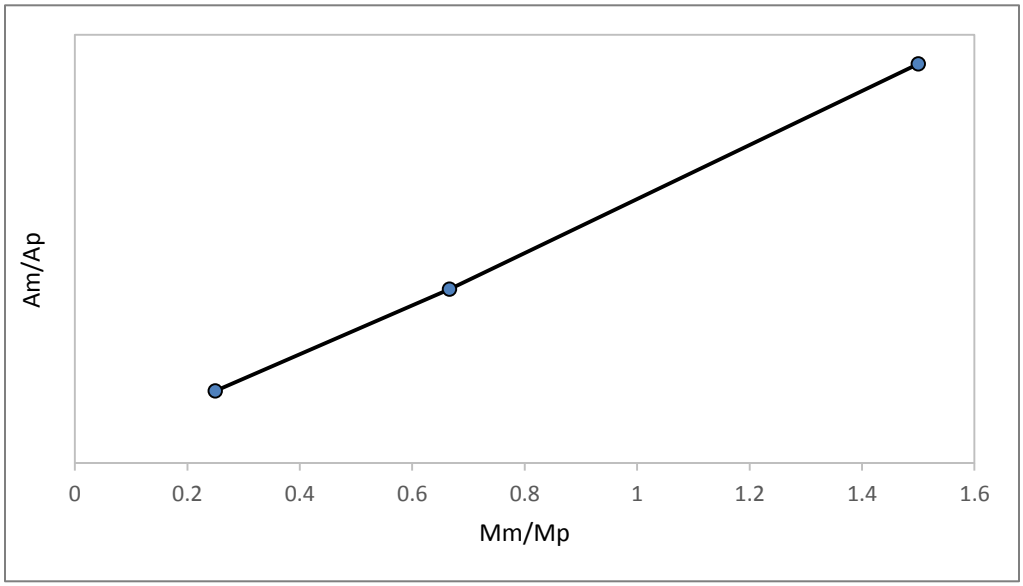


Figure 3.10 Calibration curve from internal standard method.

3.4 Catalyst Characterization Methods

The performance of any zeolite catalyst in the production of propylene from methanol process depending on its physical, chemical, thermal and structural properties. In order to analyze the results obtained, a clear understanding catalyst properties are required, which are obtained by different characterization methods. Therefore all zeolite, modified zeolite and monolith coated zeolite ZSM-5 catalysts were characterized for the physical, chemical properties, surface area, pore volume, pore size distribution, crystallinity, acidity and surface morphology. Table 3.6 describe various characterization methods used in brief.

3.4.1 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is an important technique used to measure the degree of crystallinity of the zeolite samples. The most important property of zeolite catalyst is its crystallinity. Any zeolite sample cannot be considered zeolite until there is a well-defined MFI structure of standard zeolite ZSM-5 catalyst.

The X-ray diffraction (XRD) was done on a Rigaku Miniflex diffractometer. All zeolite samples were placed on a small glass slab using a gel, the sample was placed inside the diffractometer. The analysis was done using monochromatic Cu Kα radiation source($\lambda = 1.5406*10^{-1}$ nm) at room temperature, 50 mA current, 2θ in the range of 5^o to 50^o with a step size of 0.02^o, 3^o scan/minute and electrical voltage 10 kV.

Table 3.6 Characterization Methods and Equipment Used.

Characterization Method	Parameter Measured	Equipment Used
XRD	Crystallinity	Rigaku Miniflex II diffractometer
TPD	Acidity	AutoChem II 2029 analyzer
BET Method	Surface area, pore volume, pore size distribution	Micromeritics ASAP 210 analyzer
SEM	Surface Morphology	JEOL 8200
EDX	Elemental Composition	AN10000

3.4.2 Temperature Programmed Desorption (NH_3-TPD)

Ammonia temperature programmed desorption (NH_3-TPD) analysis was carried out for the acidity measurement. Acidity is an important factor of a zeolite catalyst which reflects the product distribution in MTP process. USA made equipment AutoChem II 2029 analyzer equipped with online TCD that was used to conduct TPD analysis of all samples. Prior to TPD analysis, all samples were calcined at 500 °C for 6 hours in a furnace to remove any contaminated impurity. 0.05-0.1 gm of catalyst samples were loaded inside U- shape quartz tube and degassed at 500 °C for 3 hours by flowing Argon at 30 ml/min. The sample inside the tube cooled to 120 °C using 5% NH_3/He gas mixture flow rate of 50 ml/min. The

system was then purged using He at 100 ºC at 50 cm^3/min flow rate to remove any presence of NH_3 gas phase and adsorbed ammonia in the catalyst sample. The catalyst bed temperature was raised to 750 °C for the desorption analysis with a ramp rate of 10 °C per min. The ammonia was desorbed as the temperature elevated to 750 °C. Thermal conductivity detector monitors the concentration of NH_3 gas in the effluent.

3.4.3 BET Surface area and pore volume

Surface area is an important property of a zeolite catalyst and has pronounced effect on the gas adsorbed and on its activity as a catalyst. The surface area of the zeolite gives the idea of surface available for the catalytic reactions. The most common method used in the analysis was that developed by Brunauer-Emmett-Teller, in this method catalyst pores in a zeolite catalyst are visualized as cylindrical capillaries of different shape size and lengths. The pores of zeolite catalyst play an important role in understanding the shape selectivity. The BET surface area and pore volume of different samples were evaluated in Micromeritics ASAP 210 analyzer using N_2 adsorption at 77 K, prior to the analysis all samples were calcined to 500 °C for 6 hours to remove the presence of any impurity. 0.2 grams of sample was degassed using N_2 flow at 300 °C for 3 hours in order to remove moisture adsorbed in the pores and surface. The BET (Brunauer-Emmett-Teller) method used to calculate the total specific surface area in relative pressure p/p^o range 0.0 to 0.25. The total pore volume and pore size distribution were estimated from BJH (Barrett-Joyner-Halenda) method by adsorbed nitrogen at N_2 relative pressure p/p^o 0.99.

3.4.4 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is a technique that investigates the surface morphology of the catalyst. SEM produces clear images of specimens ranging from objects visible to the naked eye even the structures in nanometer scale.

For SEM-EDX analysis, the sample was spread on a pin stub using copper tape. The gold coating was done on the samples using cressington sputter coater for 1.5 minutes to avoid any charge build-up during the analysis and improve secondary electron signal which helps to obtain better contrast and high magnification of 100000 times.

3.4.5 Dispersive X-ray Spectroscopy (EDX)

EDX analysis was carried out during the SEM analysis to find out the elemental compositions of the zeolite or modified zeolite samples. EDX detector which is an X-ray detector used for the elemental analysis of the samples. EDX analysis is important due to the reason that we have to make sure that elemental compositions which we are reporting are right or not. The samples were prepared in the same way mentioned section 3.4.4.

3.5 Catalyst Testing

The catalytic activity of any sample for methanol conversion and propylene selectivity was investigated in a fixed bed reactor system made of stainless steel having internal diameter 21 mm and overall length 300 mm with heating length 200 mm. The reactor was designed for maximum temperature 600 °C and pressure 20 bar. Catalyst evaluation was carried out at 500 °C and 1 bar pressure, the schematic view of the experimental setup is shown in Figure 3. 4. A vertical three-zone tube furnace was the heating source of our reactor.

Before testing the catalyst activity, the parent and modified powder zeolite catalysts were filled into a die and pelletized under high pressure. The pellets were then crushed and sieved to obtain 0.5-1 mm mesh particles. For each test, 1 g of mesh catalyst was loaded into the middle of the isothermal zone of the reactor. Hydrothermally and mechanically stable zeolite coated cordierite honeycomb monolith with 400 CPSI was evaluated in the reactor system at temp 500 °C, 1 bar pressure and 15 h^{-1} WHSV.

All reactions were carried out for 2.5 hours and analyzed three times at 30, 90 and 150 minutes in an on-line GC-7890B equipped with TCD (thermal conductivity detector) having GASPRO column (60m X 320µm) and FID (flame ionized detector) having INNOWAX column (30m X 320µm X 0.5µm).

Methanol conversion, propylene selectivity and yield are calculated as [30]:

$$\text{Conversion (\%)} = \frac{\text{Mass of methanol in} - \text{Mass of methanol out}}{\text{mass of methanol in}} * 100 \qquad (3.2)$$

$$\text{Gas Selectivity (\%)} = \frac{\text{Mass of product (gas)}}{\text{Mass of gaseous hydrocarbons}} \tag{3.3}$$

$$\text{Yield (\%)} = \frac{\text{Mass of product}}{\text{Mass of methanol feed}} \tag{3.4}$$

CHAPTER 4

RESULTS AND DISCUSSION

This chapter highlights the characterization and experimental results obtained, performance and stability of zeolite, modified zeolite and monolith coated zeolite ZSM-5 catalysts. At the end, a conclusion will be drawn for the evaluation of best catalyst obtained during the study of methanol conversion to propylene over modified and monolith coated zeolite catalysts.

In the first section, the discussion starts with the study of phase, porosity, acidity and crystallinity of zeolite, modified and monolith coated zeolite catalysts. In the second section, various parameters which affect the performance of ZSM-5 including temperature, pressure and space velocity have been discussed. After discussing best catalyst in terms of SiO_2/Al_2O_3 ratio, the effect of promoters P, Ce, Fe and La on best obtained ZSM-5 catalysts for propylene selectivity and yield is discussed. Effect of the coating of best ZSM-5 catalyst on monolith support is discussed in the last of this chapter.

4.1 Catalyst Characterization

This section highlights the characterization results obtained for ZSM-5 with SiO_2/Al_2O_3 ratio of 30, 50, 80, 280 and 410, modified and monolith coated zeolite ZSM-5-280 catalysts. Modification by incipient impregnation method was done on ZSM-5-280 catalyst using promoters P, Ce, Fe and La with varying loading amount. Coating on

monolith structured support was done by dip coating method discussed earlier. XRD method was used to confirm zeolite coating while SEM technique was used to investigate the coating thickness of the single layer, double layer and triple layer coated zeolite on monolith structured support.

4.1.1 X-Ray Diffraction (XRD)

The XRD analysis was conducted to identify the crystalline phase. The XRD pattern of ZSM-5 with SiO_2/Al_2O_3 ratio of 30, 50, 80, 280 and 410 have been shown in Figure 4.1.

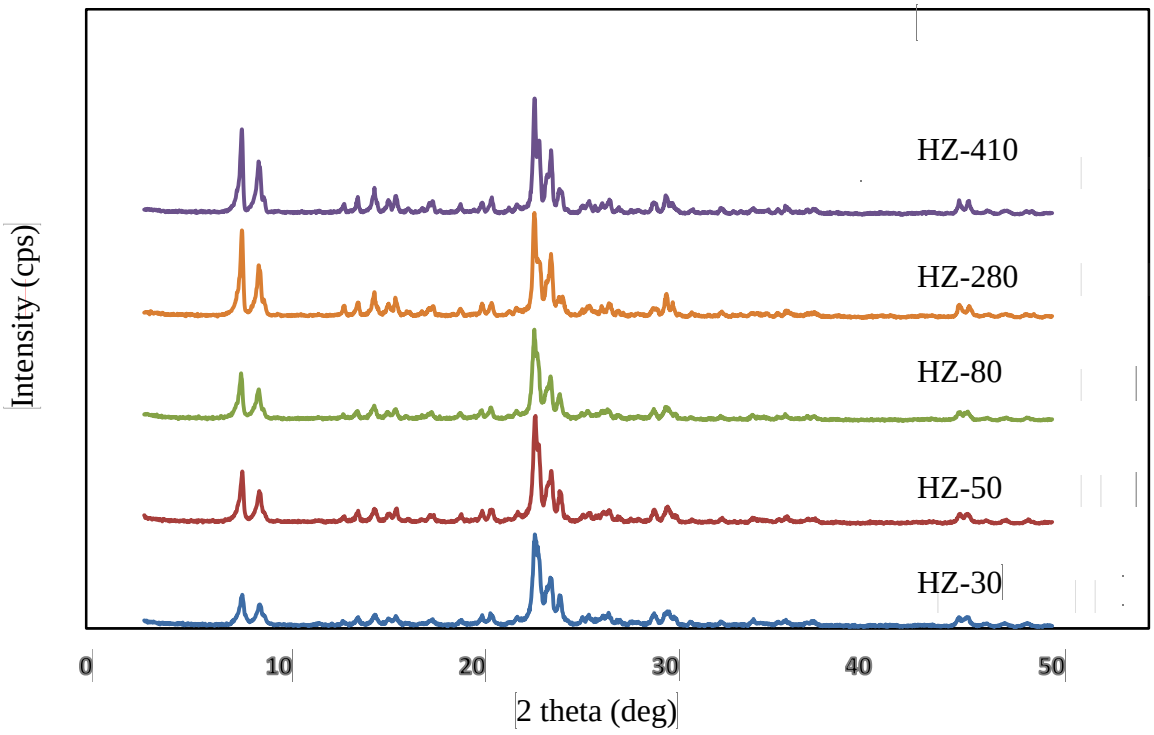


Figure 4.1 XRD pattern of zeolite HZ-30, 50, 80, 280 and 410.

The pattern obtained clearly indicates that the samples have a typical MFI structure of standard zeolite ZSM-5 catalyst with main peaks are at 2θ of 7.9, 8.8, 23.1, 23.2, 23.7 and

29.9 [97]. The XRD pattern also confirms there is no presence of any amorphous impurity in the samples.

Figure 4.2 compares XRD patterns obtained for HZ-280, 0.1P HZ-280, 0.2P HZ-280 and 0.5P HZ-280. The intensity of diffraction peaks for HZ-280, 0.1P HZ-280, 0.2P HZ-280 catalysts are almost same which confirms there is no significant change in crystallinity after P modification on parent HZ-280 catalyst. Meanwhile there is a drop in the intensity of 0.5P HZ-280 sample, this drop signifies that there is slight reduction in the crystallinity after 0.5 wt% P loading on HZ-280 catalyst.

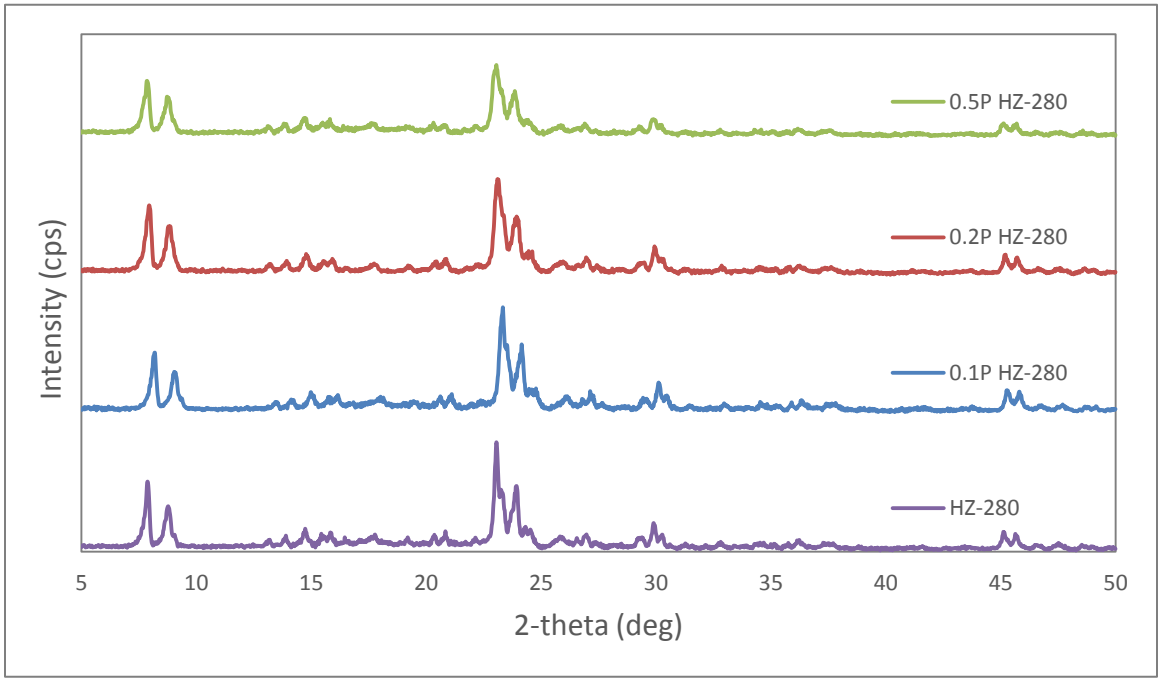


Figure 4.2 XRD patterns of HZ-280, 0.1P HZ-280, 0.2P HZ-280 and 0.5P HZ-280 catalysts.

Figure 4.3 shows XRD patterns for zeolite HZ-280, honeycomb cordierite monolith support and HZ-280 coated monolith structured catalysts. XRD pattern obtained for zeolite

coated monolith has extra peaks highlighted on the pattern confirms the presence of zeolite HZ-280 catalyst on monolith support.

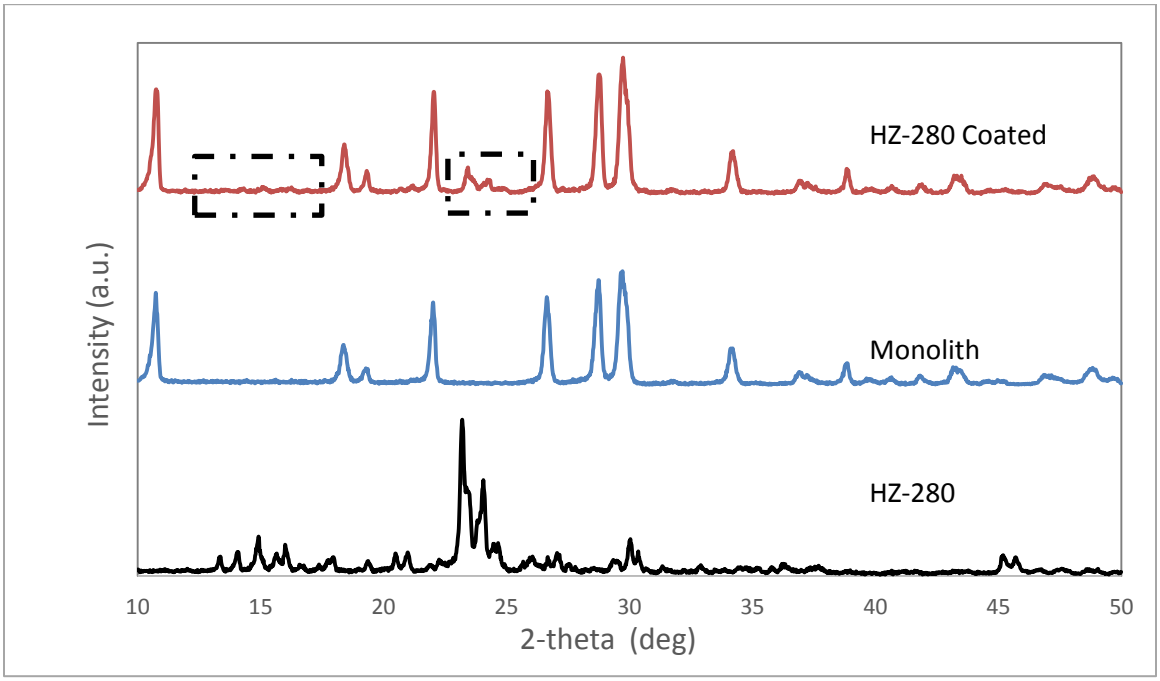


Figure 4.3 XRD patterns of HZ-280, monolith support and HZ-280 coated monolith.

4.1.2 NH_3-TPD Measurements

The results of NH_3-TPD are summarized in Table 4.1 and profile has been shown in Figure 4.4 for ZSM-5 with SiO_2/Al_2O_3 ratio of 30, 50, 80, 280 and 410. From the results in Table 4.1, it is clear that the increase in SiO_2/Al_2O_3 ratio causes decrease in strong acid sites and total acidity of catalyst. The NH_3-TPD profile of zeolite samples shows two well-resolved peaks, the first peak appears in the profile is attributed as weak acid Lewis site while the second peak as the strong acid Bronsted site [98]. The decrease in NH_3 deposition with the increase in SiO_2/Al_2O_3 ratio is due to the presence of less acidity which is clear from the deposition results of HZ-280 and 410. For high propylene production from methanol, low acidity zeolite catalysts are preferable.

A comparison of NH_3-TPD profile for parent and 0.1P modified HZ-280 catalysts are shown in Figure 4.5. The P-modified catalyst has similar TPD profile comparing to the parent catalyst sample but there is a shift of strong acid site from temperature 450 to 440 °C. The acidity obtained for HZ-280 is 0.054 mmol/g of catalyst and 0.1P HZ-280 is 0.031 mmol/g of catalyst. The results reveal that there is the partial elimination of strong acid sites after P modification of zeolite HZ-280 catalyst.

Table 4.1 Acidity observation of zeolites.

SiO_2/Al_2O_3	Acidity (mmol/g)			W/S ratio
	Weak	Strong	Total	
30	0.36	0.22	0.58	1.33
50	0.18	0.15	0.32	1.20
80	0.08	0.07	0.15	1.14
280	0.031	0.054	0.085	0.6
410	0.005	0.02	0.025	0.2

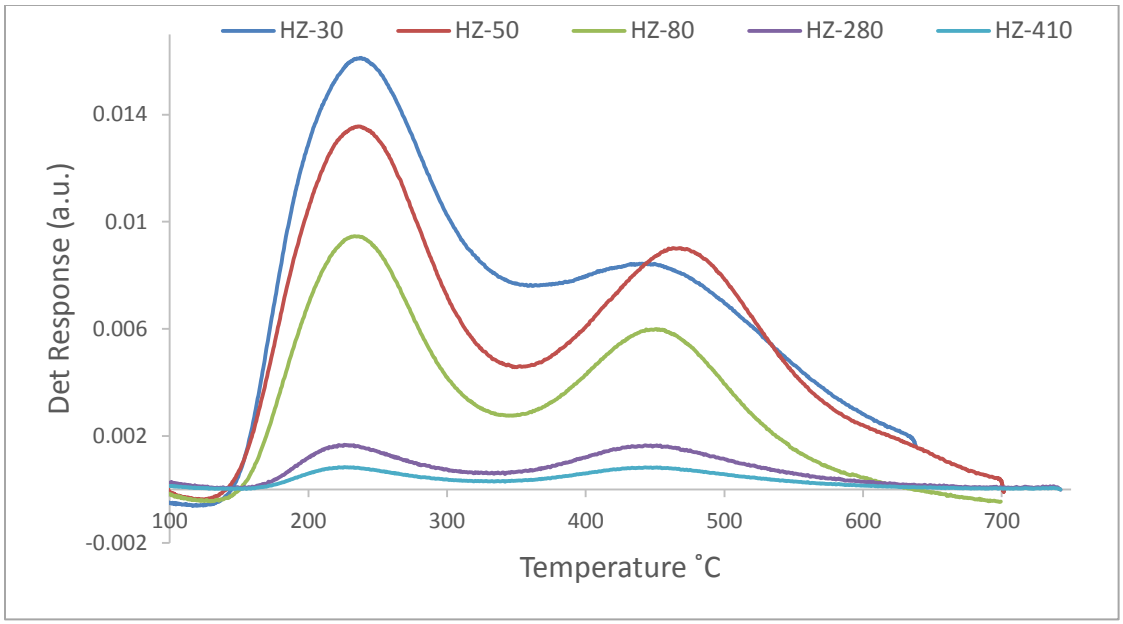


Figure 4.4 NH_3-TPD profile of HZ-30, 50, 80 & 280.

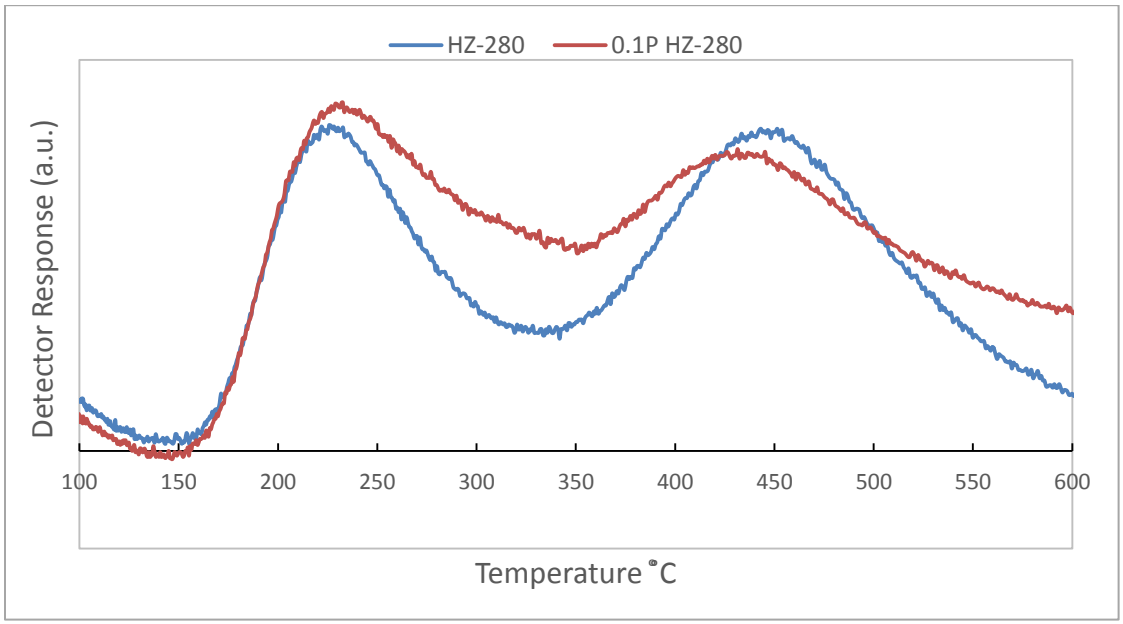


Figure 4.5 NH_3-TPD profile of ZSM-5-280 and 0.1P ZSM-5-280.

4.1.3 BET Surface Area, Pore volume and Pore size Distribution.

The BET surface area results are shown in Table 4.2. Textural properties reveal that the increase in SiO_2/Al_2O_3 ratio of ZSM-5 develops more micropores and reduces mesopores which result in a reduction of pore average diameter which improves olefins production. The surface area of all samples are in the range of 300 to 400 m^2/gm of catalyst, this reflects high surface area is the property of a zeolite catalyst. The N_2 adsorption – desorption isotherm plots and pore size distribution for HZ-30, 50, 80, 280, 0.1P HZ-280 have been shown in Figure 4.6 to Figure 4.10.

Table 4.2 Textural data obtained from BET analysis.

Sample	A_{BET} (m^2/g)	A_M (m^2/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	V_{total} (cm^3/g)	D_{AA} (nm)
HZ-30	308.6	202.8	0.098	0.122	0.207	6.4
HZ-50	340.8	190.6	0.093	0.154	0.225	7.3
HZ-80	342.8	177.1	0.086	0.134	0.220	4.4
HZ-280	390.1	329.6	0.152	0.056	0.209	2.8
0.1P HZ-280	384.9	324.0	0.144	0.067	0.211	2.5

A_{BET} : BET surface area, A_M : micropore area, V_{micro} : micropore volume, V_{meso} : mesopore volume, V_{meso} : total pore volume, D_{AA} : adsorption average pore diameter.

From the results for parent and 0.1P modified zeolite HZ-280 in Table 4.2, it can be seen that there is an only slight change in the total surface area, micro-pore surface area and pore volume of P-modified HZ-280 to the parent HZ-280 catalyst, this indicates there is no considerable change in MFI structure of the zeolite catalyst. There is an increase in the mesoporosity and there is a decrease in average pore diameter of P-modified HZ-280 which

results in fewer aromatics formation. It is believed that the aromatics formed during the reaction diffuse back and would have been dissociate to olefins and hence improves the olefins selectivity after P modification of HZ-280 catalyst.

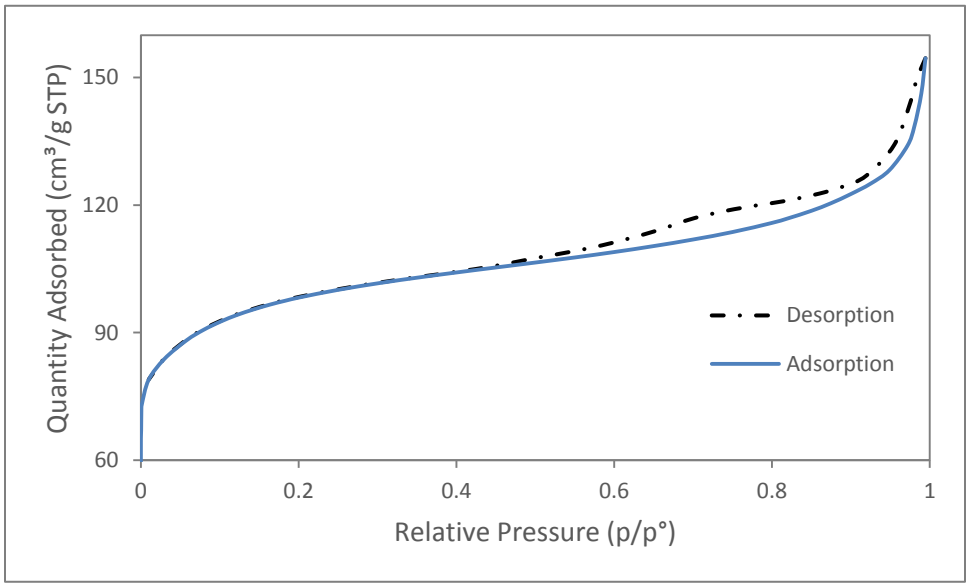


Figure 4.6 N_2 adsorption desorption plot for HZ-30.

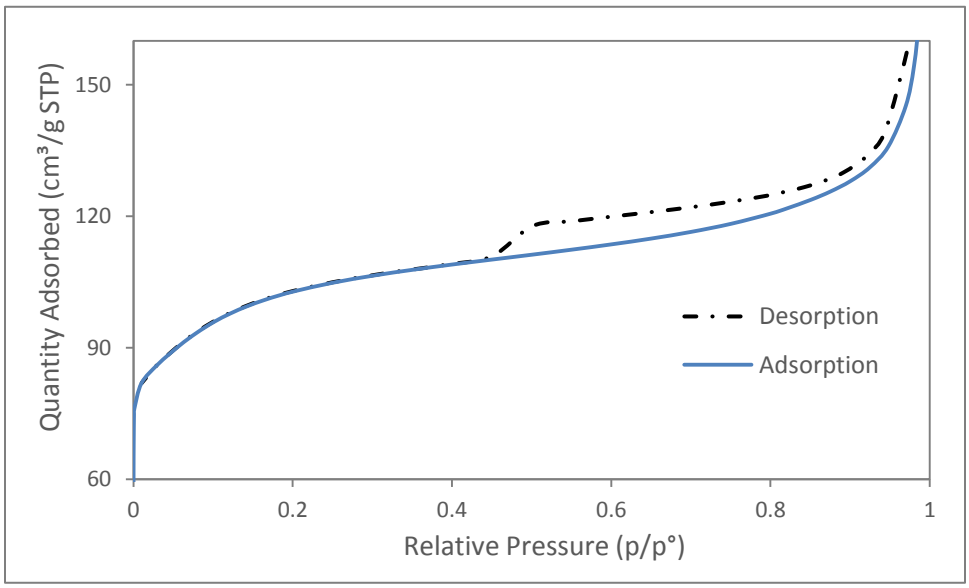


Figure 4.7 N_2 adsorption desorption plot for HZ-50.

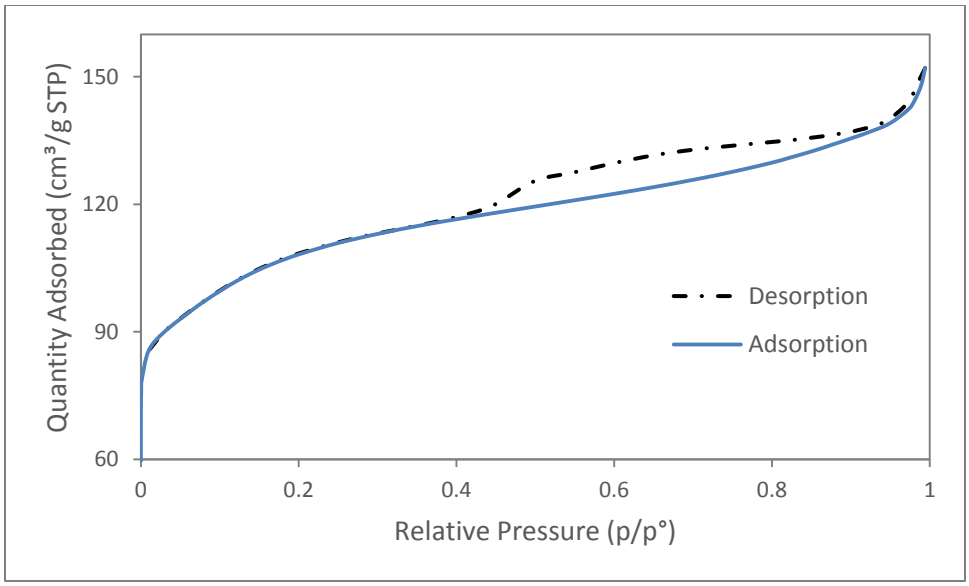


Figure 4.8 N_2 adsorption desorption plot for HZ-80

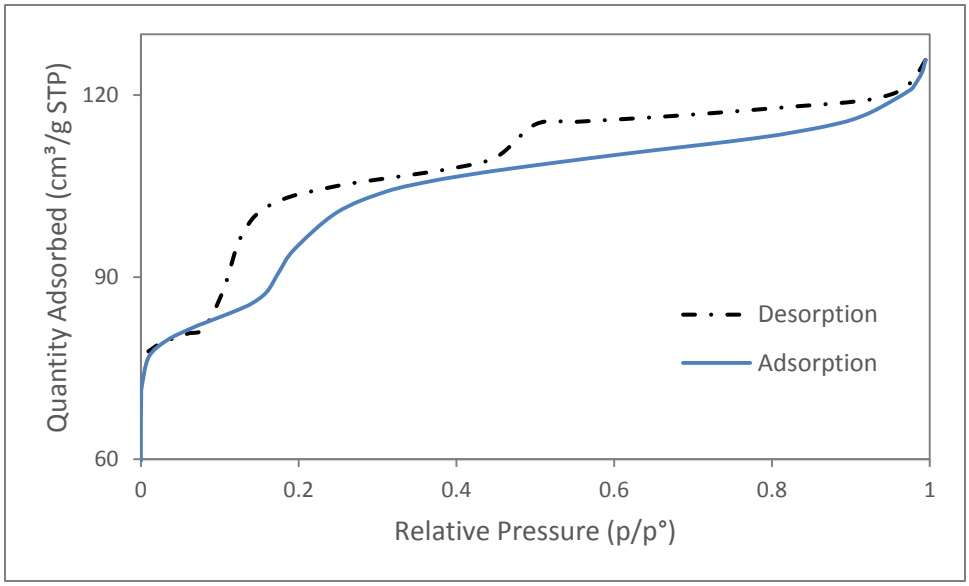


Figure 4.9 N_2 adsorption desorption plot for HZ-280

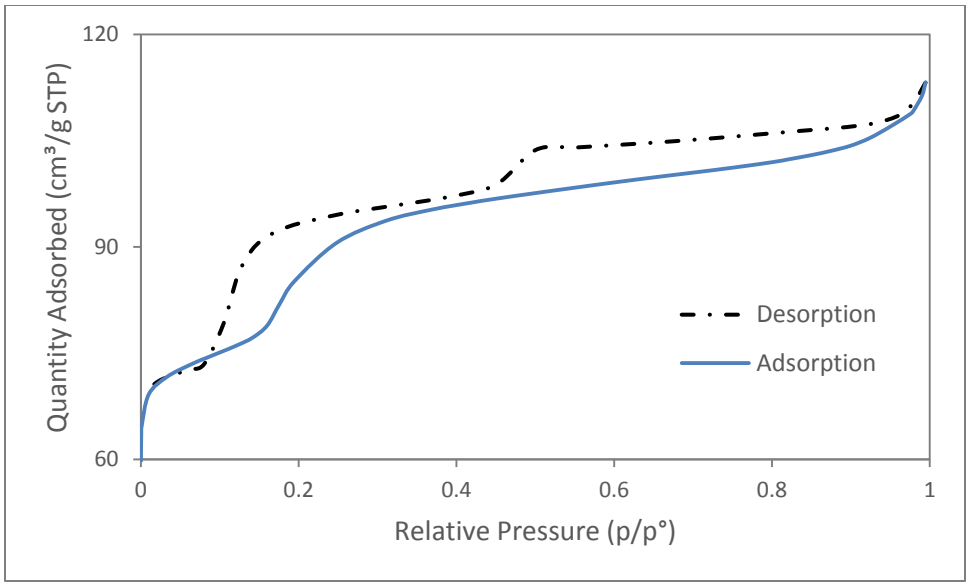


Figure 4.10 N_2 adsorption desorption plot for 0.1P HZ-280

4.1.4 SEM and EDX Analysis

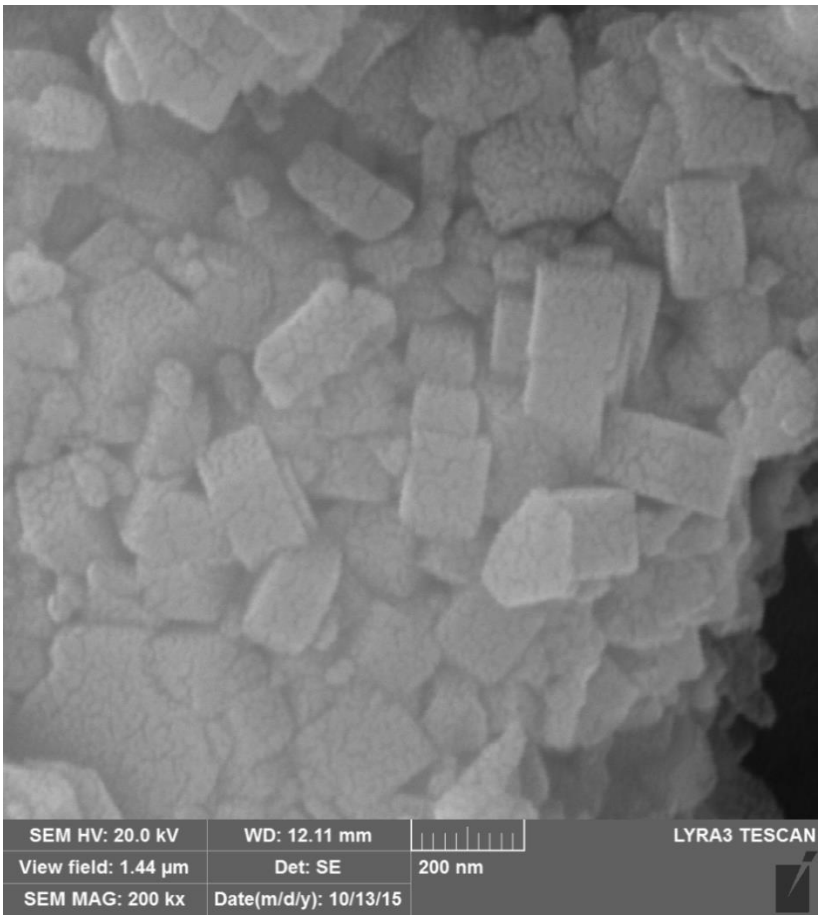
Figure 4.11 to Figure 4.15 shows the surface morphology and EDX spectrum of ZSM-5 with SiO_2/Al_2O_3 ratio of 30, 50, 80, 280 and 410. Crystallinity is an important property of zeolite catalysts. Crystal size shows a significant improvement in propylene selectivity during MTP reaction. The images highlight the high crystallinity of all zeolite samples. The crystals are either cubical or elliptical in shape with uniform size distribution. The samples are free from any kind of amorphous impurities. High agglomeration has been observed in HZ-30 and HZ-50. The approximate crystal sizes are 0.15, 0.2, 0.45 and 0.7 µm for SiO_2/Al_2O_3 ratio of 30, 50, 80 and 280.

Figure 4.16 is the SEM image of 0.1P modified HZ-280 catalysts. Sometimes modification affects the crystallinity of the catalyst, but after 0.1 wt% P modification on HZ-280 catalyst there is no effect on the crystallinity of the catalyst. Crystallinity remains unaltered even after P loading.

The EDX analysis of all samples is tabulated below in Table 4.3. The EDX results confirm the presence of Si and Al with O. The first peak is the peak of gold used in the coating of samples to avoid any charge build-up during the analysis. The SiO_2/Al_2O_3 ratio obtained by EDX analysis are nearly same claimed by ZEOLYST.

Table 4.3 EDX analysis results.

Sample	**Elemental Weight (%)**			**SiO_2/Al_2O_3**
	Si	**Al**	**P**	
HZ-30	36.41	2.22	-	32
HZ-50	30.24	1.16	-	50
HZ-80	31.74	0.77	-	79
HZ-280	45.12	0.28	-	311
HZ-410	45.37	0.21	-	417
0.1P HZ-280	41.60	0.25	0.09	332
0.2P HZ-280	44.31	0.33	0.29	269
0.5P HZ-280	40.35	0.20	0.63	403



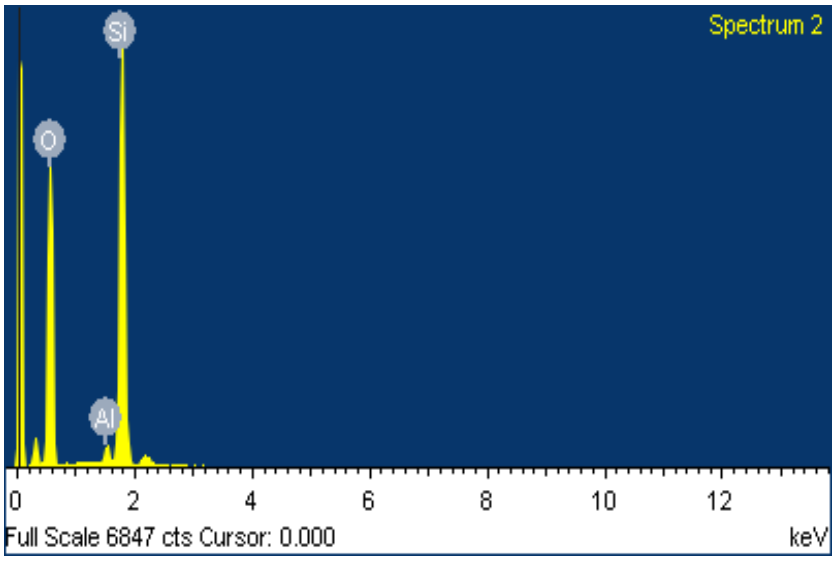
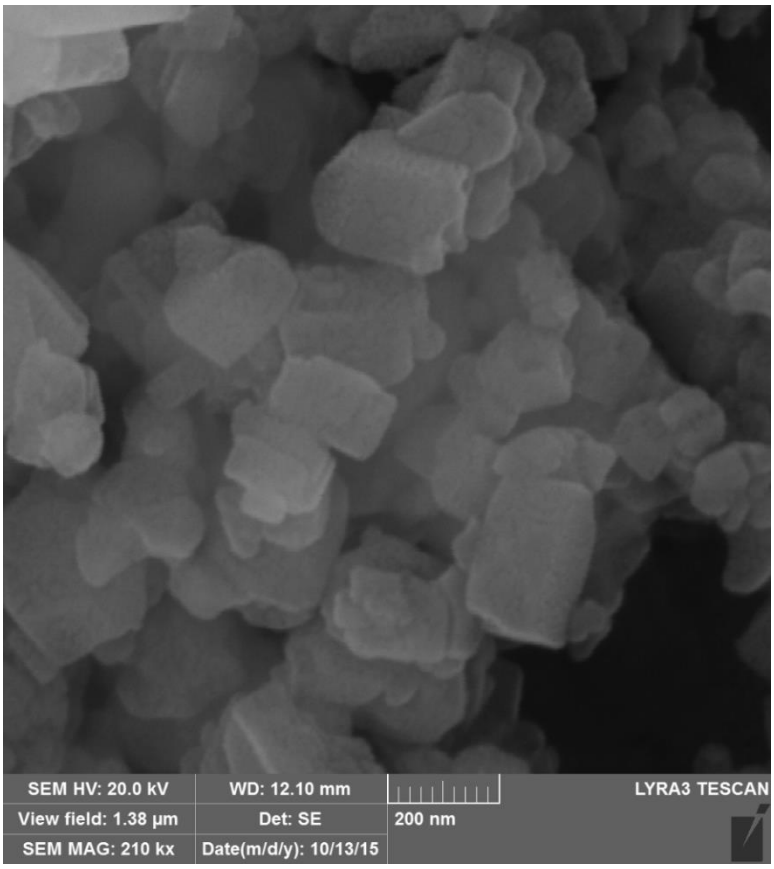


Figure 4.11 SEM image and EDX spectrum of HZ-30.



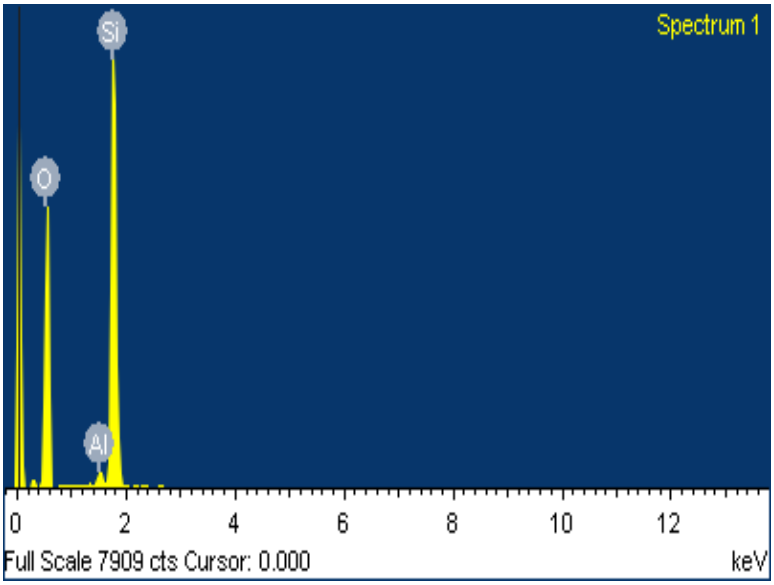
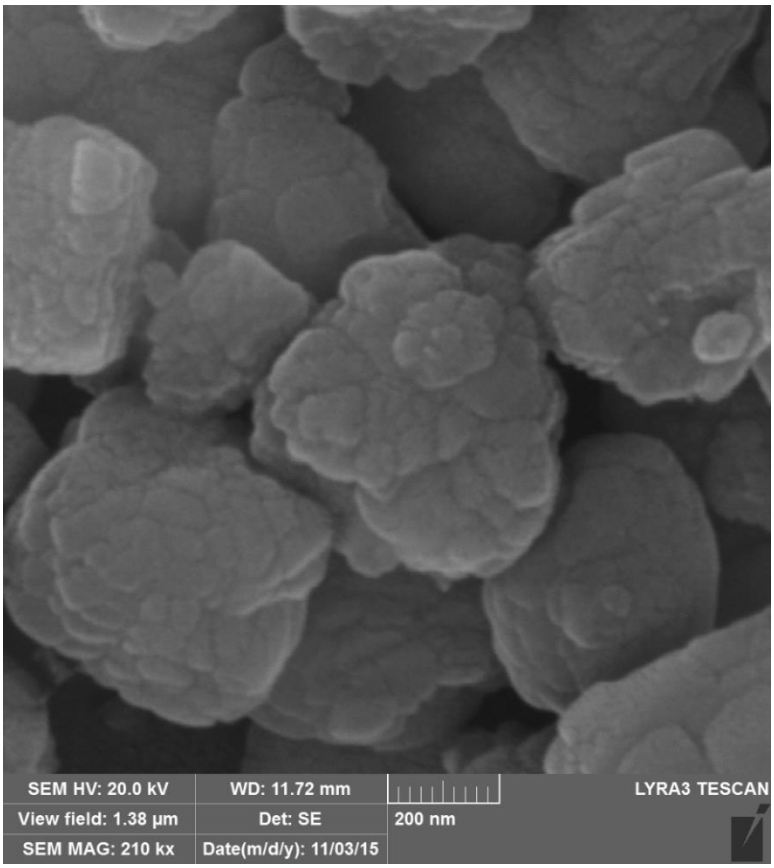


Figure 4.12 SEM image and EDX spectrum of HZ-50.



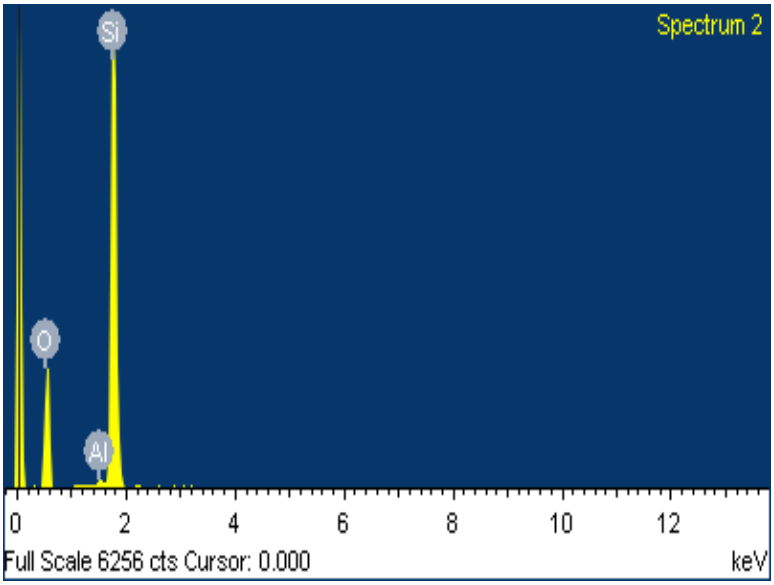
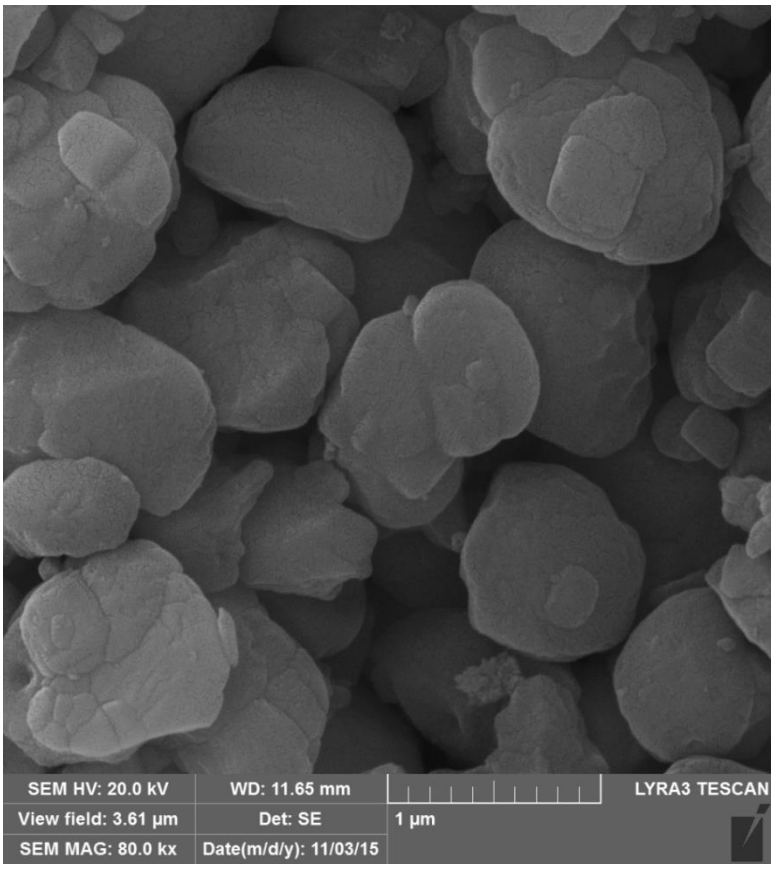


Figure 4.13 SEM image and EDX spectrum of HZ-80.



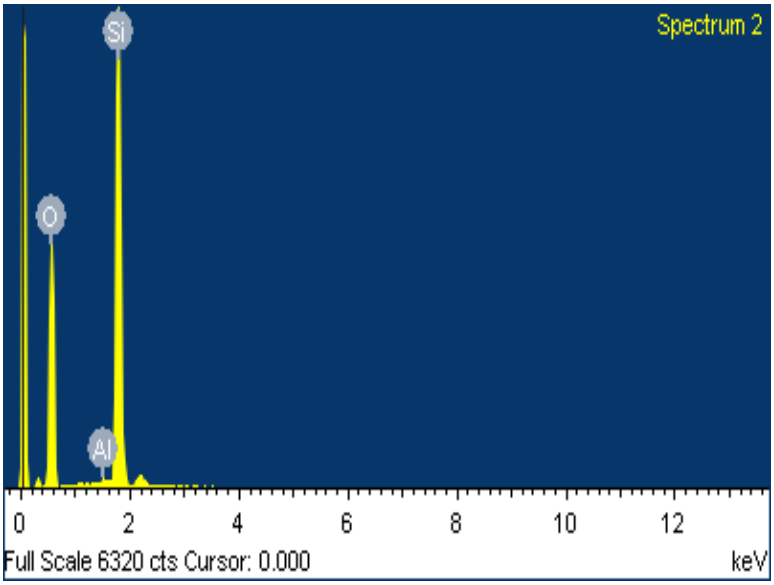


Figure 4.14 SEM image and EDX spectrum of HZ-280.

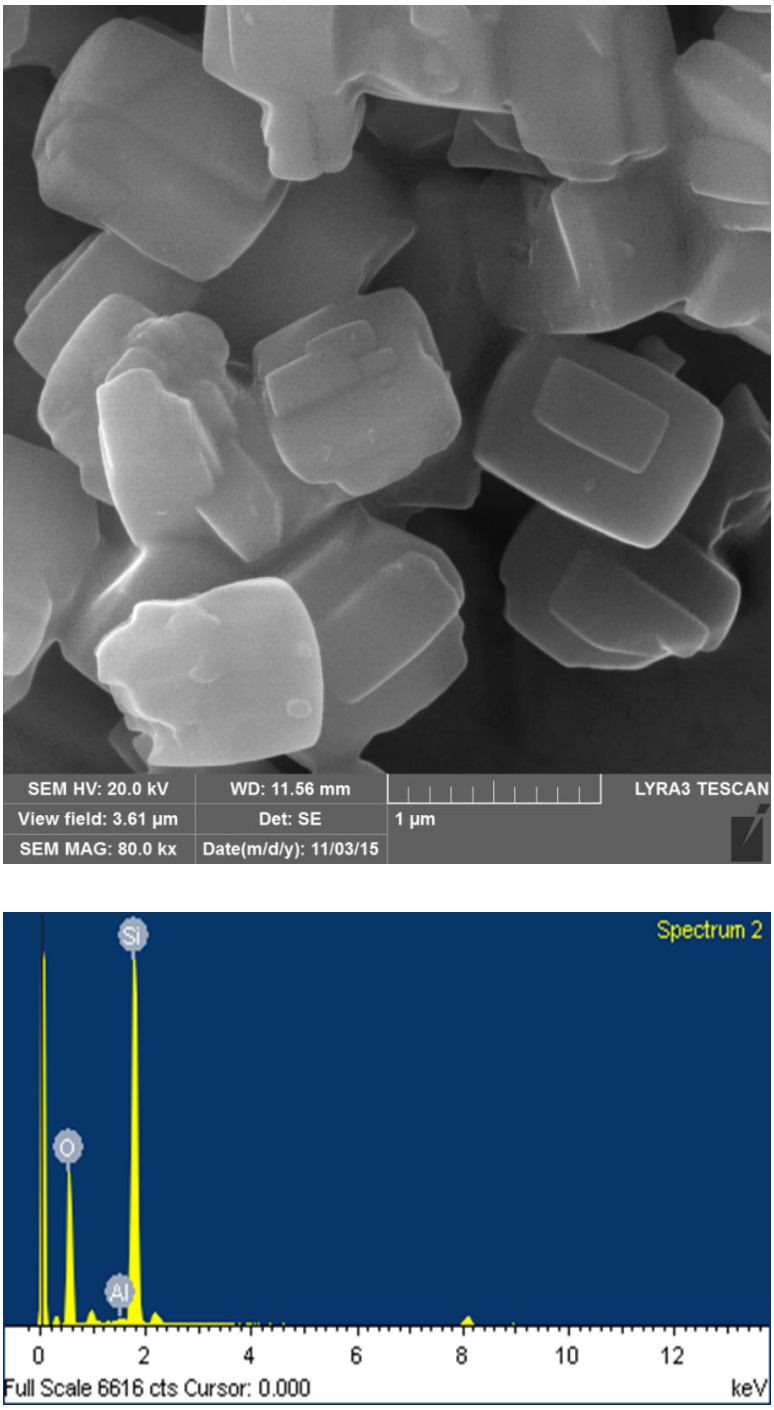


Figure 4.15 SEM image and EDX spectrum of HZ-410.

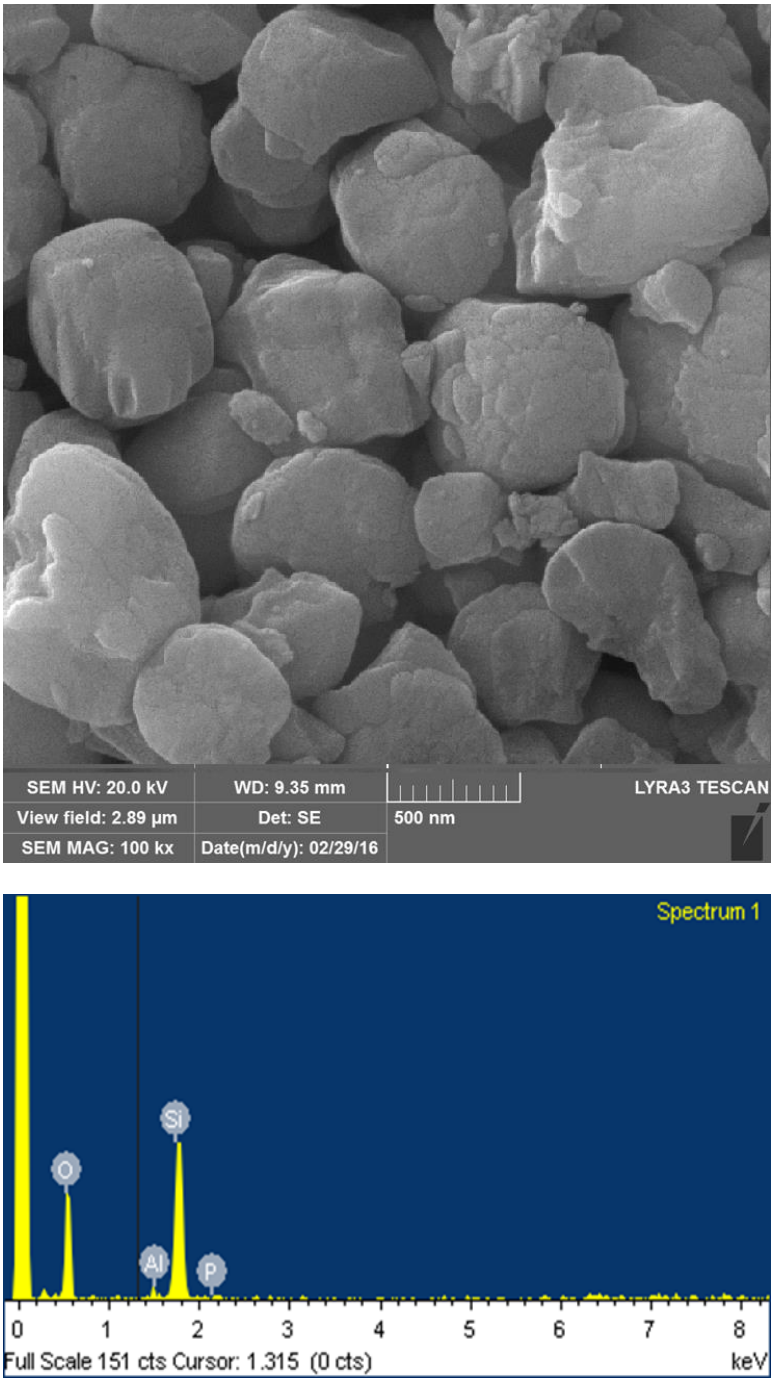


Figure 4.16 SEM image and EDX spectrum of 0.1P HZ-280.

Figure 4.17 shows the surface morphology of the honeycomb monolith support. The images clearly indicate the macroporous nature of monolith support on which the zeolite can diffuse and remain stick without any abrasion. The average thickness of monolith wall is found to be 195 µm while the average length between the walls of a channel is 1006 µm.

Figure 4.18 shows the single layer monolith coated zeolite HZ-280 catalyst. The images indicate that there is no change in the surface morphology of the zeolite after coating with 1% binder (Ludox AS-40). It can be seen clearly that the zeolite dispersed uniformly on the surface of monolith without leaving any big area uncoated. Figure 4.19 shows the SEM images obtained for the double layer and triple layer monolith coated HZ-280 catalysts, it can be seen that there is an increase in coating thickness from single to double layer than in triple layer. The zeolite coating thickness for single layer, double layer and triple layer monolith coated HZ-280 catalysts are obtained to be 4.2 µm, 6.8 µm and 10.4 µm.

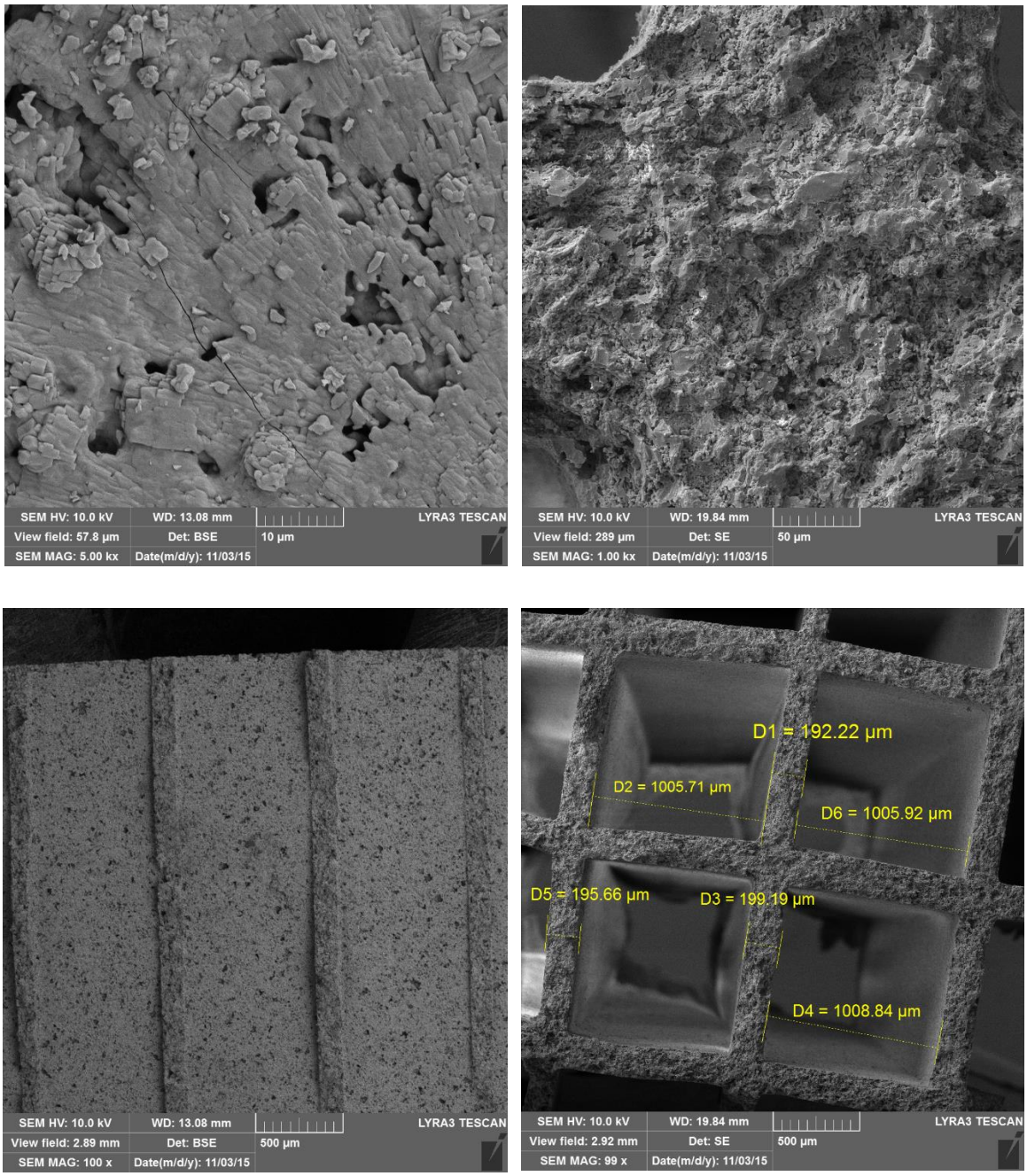


Figure 4.17 SEM images of cordierite honeycomb monolith support.

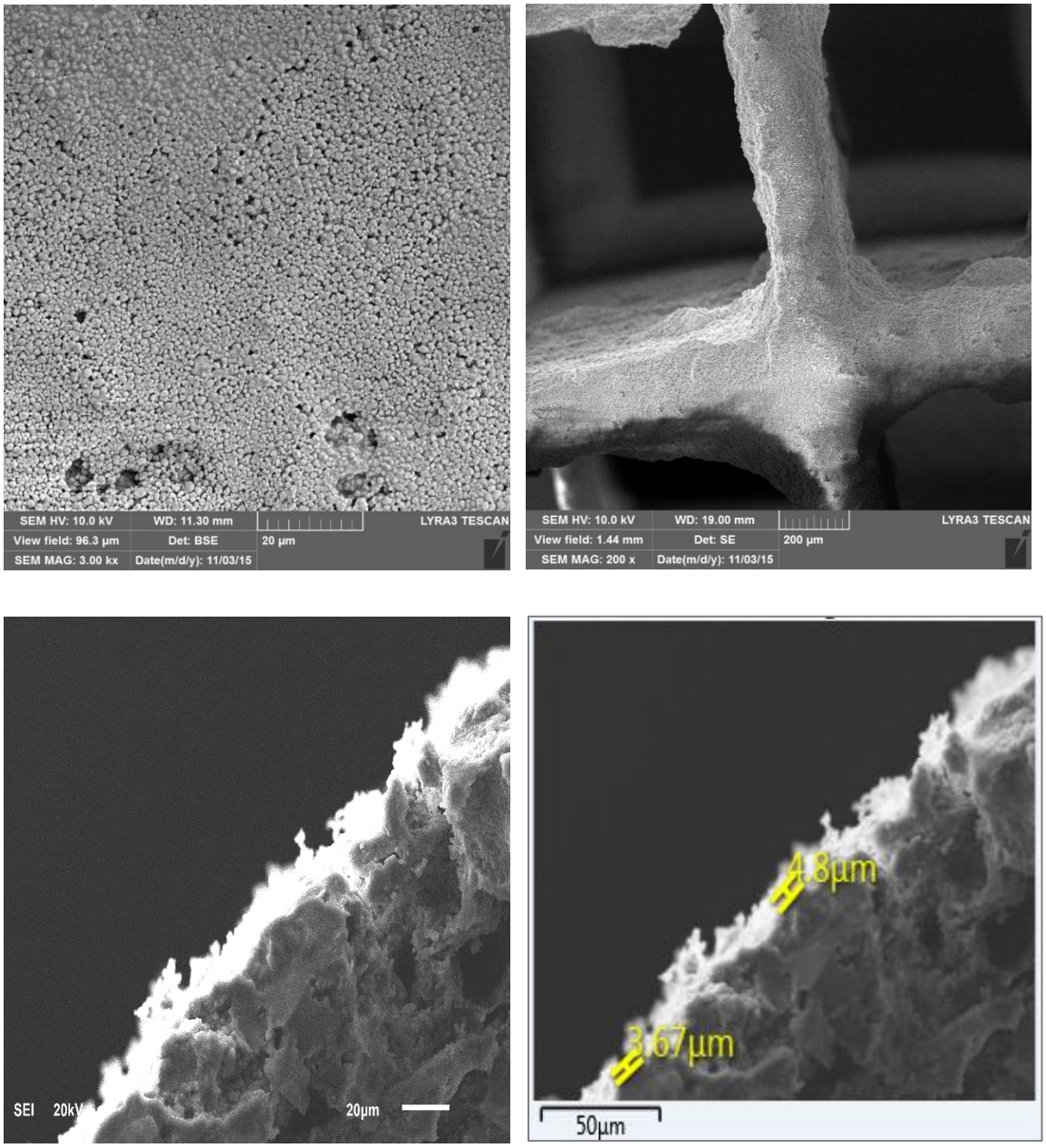


Figure 4.18 SEM images of single layer HZ-280 coated monolith catalyst.

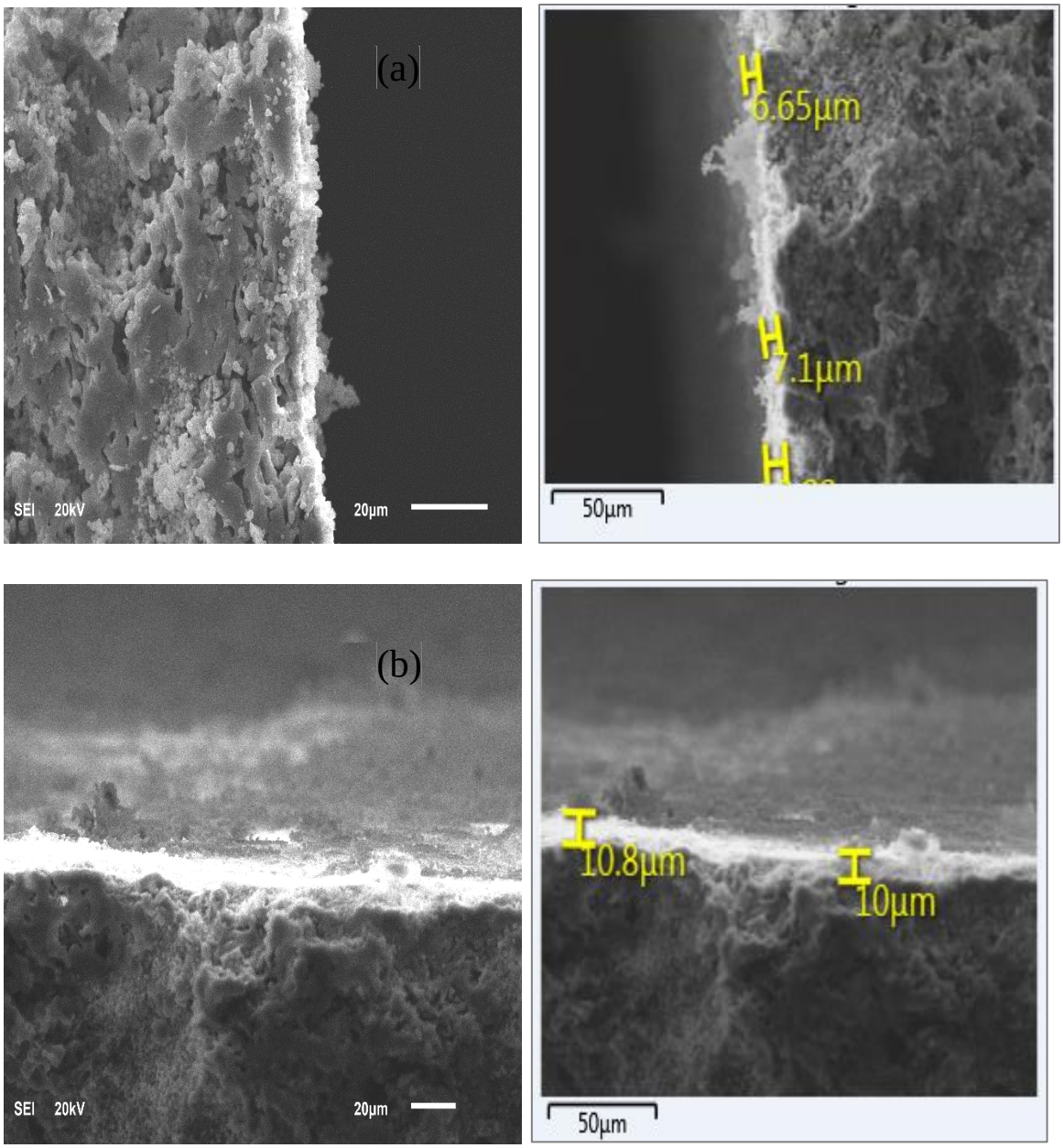


Figure 4.19 SEM images of (a) double layer, (b) triple layer HZ-280 coated monolith catalyst.

4.2 Catalyst Evaluation

This section of chapter 4 enlighten the catalytic activity of zeolite, modified zeolite, monolith coated zeolite and modified monolith coated zeolite catalysts. At the end, comparison of parent, P-modified and monolith coated catalysts have been drawn for methanol conversion and propylene selectivity based on 41.5 hours. It starts with the discussion of preliminary experimental results which include the effect of methanol/N_2 feed and catalyst/SiC ratios, then the effect of temperature and pressure on catalytic performances. All experiments were carried in a fixed bed reactor system. In the start of the study catalytic activity of zeolites ZSM-5 with SiO_2/Al_2O_3 molar ratio of 30, 50, 80, 280 and 410 were investigated first. Temperature, pressure, space velocity are typical process variables of the reaction system.

4.2.1 Preliminary Experiments

Preliminary experiments were conducted by varying temperature, pressure, methanol flow, methanol/nitrogen ratio and catalyst/SiC ratio. Since methanol/N_2 and catalyst/SiC ratio play an effective role in methanol conversion to propylene selectivity, therefore, it was important to fix these two parameters for next experiments. From the literature usually methanol conversion has been done at high temperature and low pressure [16], [99]–[104]. To see the effect of methanol/N_2 and catalyst/SiC ratios high temperature 500 °C and low-pressure 1bar, operating conditions were used. Best results were obtained at Catalyst : Sic ratio 1:4 and nitrogen flow rate 44 ml/min at space velocity 15 h^{-1}. For

further studies of the effect of temperature, effect of pressure and effect of space velocity these two parameters remained constant.

4.2.2 Reproducibility Check

In order to establish the reliability of the reaction setup, sampling, and analytical procedures, reproducibility checks were carried out for HZ-280 and 0.1P HZ-280 catalysts at WHSV 15 h^{-1}. The results are shown in Figure 4.20 and error is tabulated in Table 4.4.

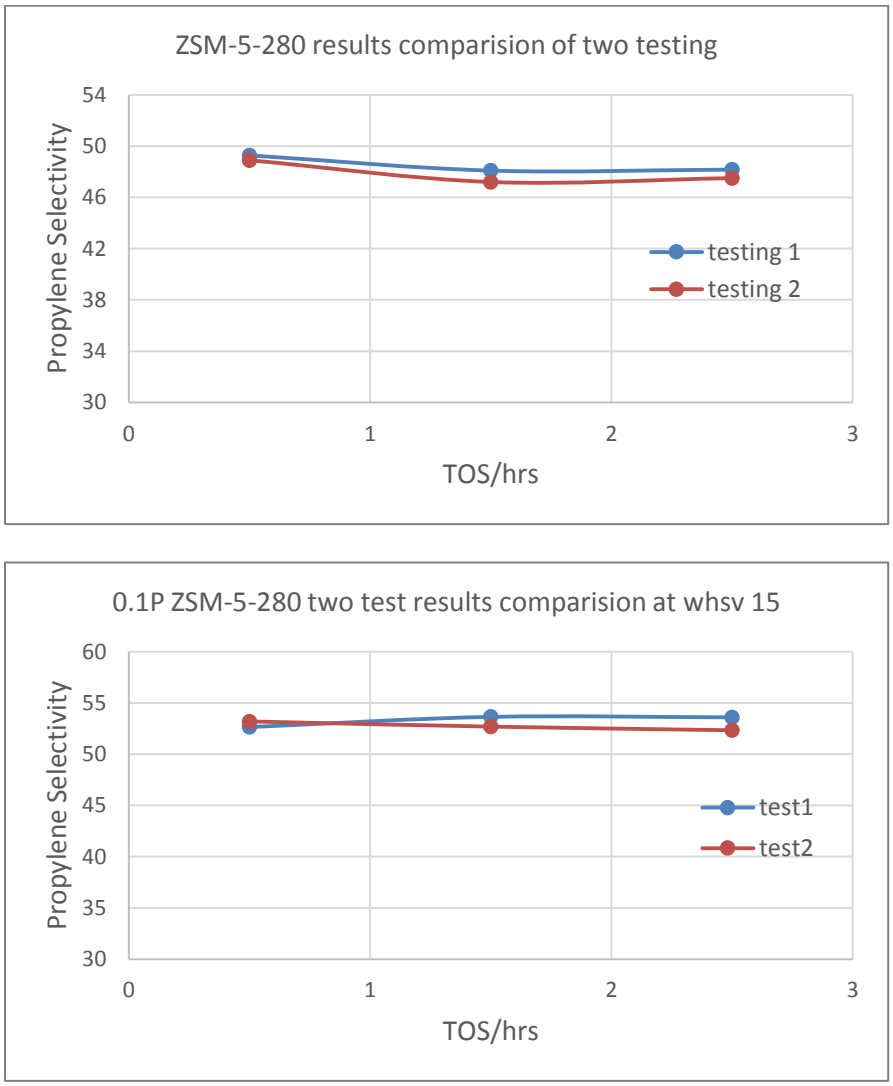


Figure 4.20 Reproducibility check for HZ-280 and 0.1P HZ-280.

Table 4.4 Error table.

Sample	Error
HZ-280	
Conversion	0.3
Propylene Selectivity	0.6
0.1P HZ-280	
Conversion	0
Propylene Selectivity	0.9

4.2.3 Effect of Temperature and Pressure

The catalytic activity of a zeolite catalyst is affected by temperature and pressure. There is a pressure drop in a packed bed pelletized catalyst, this pressure drop results in side reactions mainly oligomerization of olefins which results in more aromatics generation and drop in propylene selectivity. Temperature is a prominent parameter and has pronounced effect on the product distribution in the conversion of methanol to hydrocarbons. Selectivity has been found to be favored by high temperatures largely due to cracking reactions [23], [105]. High temperature also causes decomposition of methanol to methane [106]. The effect of temperature and pressure was studied on zeolite HZ-280 at WHSV 15 h^{-1}. The reaction was also done at temperatures 400, 450 and 500 °C. MTP is a low pressure operation, to justify this the reaction was carried out at three different pressures 1, 2 and 3 bars. Figure 4.21 shows the effect of temperature and pressure, from the results obtained it

can be seen that there is a prominent effect of pressure on methanol conversion and propylene selectivity, therefore the reaction was carried out at 1 bar pressure.

Table 4.5 Reaction conditions for MTP.

Temperature	500 °C
Pressure	1 bar
Flow rate of N_2	44 ml/min
Catalyst : SiC	1:4

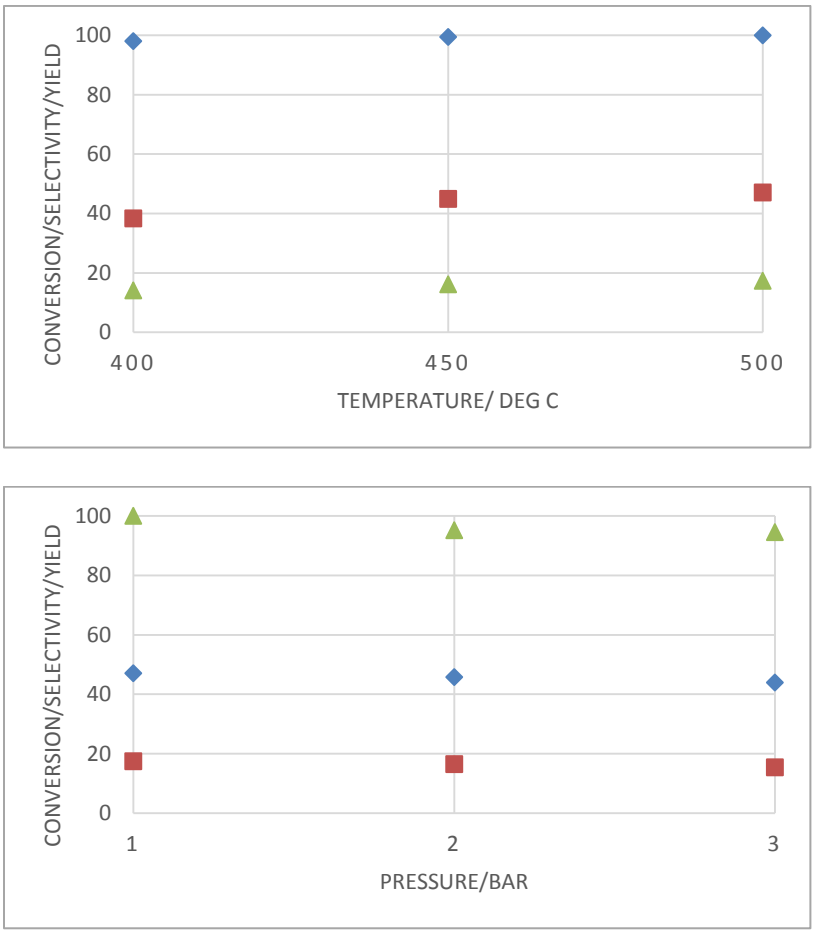


Figure 4.21 Effect of temperature and pressure on methanol conversion, propylene selectivity and yield for HZ-280 at WHSV 15h^{-1}.

Temperature could be chosen from 450 to 500 °C, for further study 500 °C temperature and 1 bar pressure was selected. So the operating conditions selected for further studies are tabulated in Table 4.5.

4.2.4 Effect of Weight Hourly Space Velocity

Space velocity is another important parameter in methanol conversion to propylene studies. The effect of space velocity on the performance of zeolite ZSM-5 with SiO_2/Al_2O_3 ratio of 30, 50, 80, 280 and 410 was studied at optimum operating conditions discussed in section 4.2.1 and 4.2.3. Experiments were carried out at various space velocities to investigate its effect on the HC's product distribution.

It is a well-known fact that space velocity has a considerable effect on the HC's product distribution [44]. Generally, selectivity of olefins can be enhanced by low residence time [106]. Technically this is correct, because high space velocity will reduce the contact time of reactant molecules on the active sites of a catalyst which will result in a drop of methanol conversion. The study was conducted at methanol feed flow rate 0.24 to 0.40 ml/min i.e. WHSV 11 to 19 h^{-1}.

The results obtained are tabulated in Table 4.6, 4.7 and 4.8, from the experimental results obtained it can be concluded that the best results in terms of methanol conversion, propylene selectivity and yield are at WHSV 15 h^{-1}. Space velocity at 11 gave low propylene comparing to space velocity 15 while at space velocity 19 there was a drop in methanol conversion which results in a drop in propylene yield. It can also be concluded that HZ-280

was the best performing catalyst at space velocity 15. The effect of space velocity on propylene selectivity and yield for all catalysts is shown in Figure 4.22.

Table 4.6 Experimental results obtained at WHSV 11 h^{-1}.

SiO_2/Al_2O_3	**30**	**50**	**80**	**280**
Conversion (%)	88	94	99	99
Selectivity (%)				
C_1	18.0	10.8	4.7	0.6
C_2^-	1.2	1.0	1.1	0.2
$C_2^=$	14.2	14.4	28.5	13.1
C_3^-	3.3	3.9	4.2	1.9
$C_3^=$	**26.0**	**32.2**	**31.1**	**47.8**
$C_4^=$	17.0	14.4	18.7	26.4
C_{4-5}	20.4	23.4	11.7	8.9
$C_{5+}^=$	0	0	0	0.5
$C_3^=/ C_2^=$	1.8	2.2	1.1	3.7
Yield (%)				
$C_2^=$	3.0	3.0	6.2	2.7
$C_3^=$	**8.1**	**10.0**	**10.2**	**15.8**
$C_4^=$	7.0	6.0	8.1	10.8
Aromatics	7.2	6.0	4.0	2.9
Water + DME	62.2	59.0	55.9	61.4
Mass Balance	95	96	94	98

Reaction conditions: T=500 °C, P= 1bar and time of stream 2.5 hours.

Table 4.7 Experimental results obtained at WHSV 15 h^{-1}.

SiO_2/Al_2O_3	**30**	**50**	**80**	**280**	**410**
Conversion (%)	100	98	98	100	88
Selectivity (%)					
C_1	9.1	8.4	8.6	0.3	0
C_2^-	2.3	2.0	0.8	0.2	0.1
$C_2^=$	18.1	18.2	15.6	11.8	10.8
C_3^-	9.1	6.6	3.4	2.1	1.4
$C_3^=$	**21.6**	**27.6**	**37.8**	**47.3**	**49.2**
$C_4^=$	9.9	10.7	18.7	28.7	31.1
C_{4-5}	29.9	26.5	15.1	8.0	6.4
$C_{5+}^=$	0	0	0	1.6	1.0
$C_3^=/ C_2^=$	1.2	1.5	2.4	4.1	4.6
Yield (%)					
$C_2^=$	4.6	4.4	3.8	3.1	4.9
$C_3^=$	**8.3**	**10.0**	**13.0**	**17.4**	**16.4**
$C_4^=$	5.1	5.1	9.2	14.0	9.7
Aromatics	8.0	6.3	4.0	2.4	1.7
Water + DME	54.6	55.5	54.9	54.5	56.9
Mass Balance	97	97	94	97	96

Reaction conditions: T=500 °C, P= 1bar and time of stream 2.5 hours.

Table 4.8 Experimental results obtained at WHSV 19 h^{-1}.

SiO_2/Al_2O_3	**30**	**50**	**80**	**280**
Conversion (%)	95	92	100	98
Selectivity (%)				
C_1	10.6	9.5	4.0	0.6
C_2^-	1.3	1.2	0.9	0.2
$C_2^=$	16.7	16.2	19.0	12.4
C_3^-	4.8	5.0	7.1	1.8
$C_3^=$	**29.9**	**30.5**	**35.4**	**48.2**
$C_4^=$	11.6	13.4	18.0	28.4
C_{4-5}	24.8	24.3	14.4	7.9
$C_{5+}^=$	0	0	0	0.5
$C_3^=/ C_2^=$	1.8	1.9	2.0	3.9
Yield (%)				
$C_2^=$	3.4	3.2	4.3	2.7
$C_3^=$	**9.0**	**9.0**	**11.8**	**16.1**
$C_4^=$	4.6	5.3	8.0	13.6
Aromatics	6.3	4.7	4.0	2.0
Water + DME	59.2	59.9	55.2	56.7
Mass Balance	95	96	95	98

Reaction conditions: T=500 °C, P= 1bar and time of stream 2.5 hours.

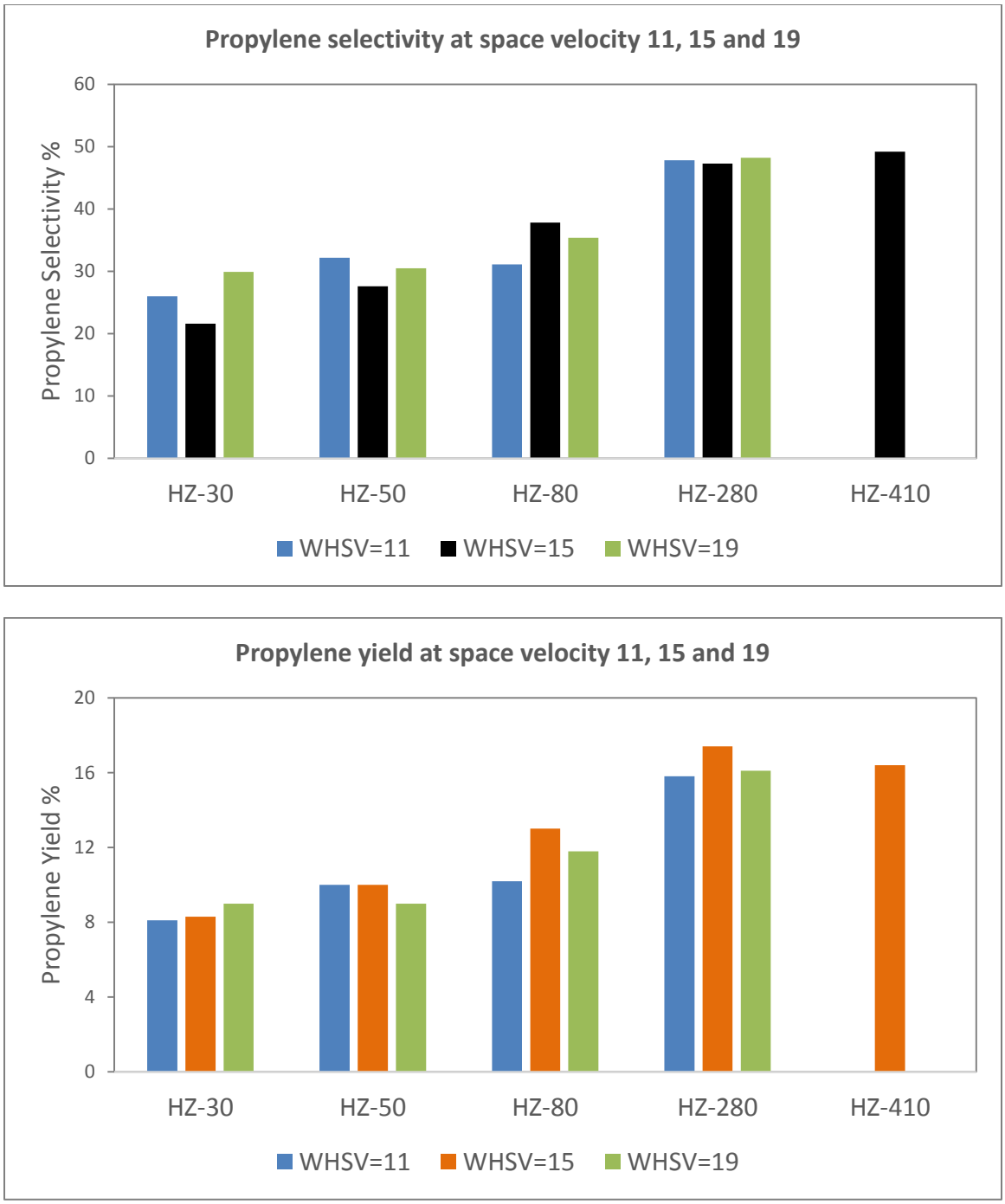


Figure 4.22 Propylene selectivity and yield at space velocities 11, 15 and 19 h^{-1}.

4.2.5 Effect of SiO_2/Al_2O_3 ratio

SiO_2/Al_2O_3 ratio significantly influences the product distribution in MTP process (Table 4.9), there is an increase in propylene selectivity and yield at optimized conditions i.e. 500 °C temp, 1 bar pressure and WHSV of 15 h^{-1}. Strong acid sites cause aromatization of olefins [107], [108] in MTP reaction thus aromatics are considered as an enemy of olefins generation and the results from Table 4.9 clearly indicates that the increase in SiO_2/Al_2O_3 ratio causes low aromatics formation which improves the olefin selectivity. ZSM-5 with SiO_2/Al_2O_3 ratio 280 gave best results with 47.3% propylene selectivity and 17.4% propylene yield with 100% methanol conversion. It can also be seen that there is a substantial drop in alkanes formation with high SiO_2/Al_2O_3 ratio due to decrease in strong acid sites, it also suppresses the side reactions causing coke formation. The activity of acid sites of zeolite is reduced constantly due to coke formation and hence affecting the performance of the catalyst [109]. High acidity catalysts can be considered if the target are alkanes and aromatics. Very high SiO_2/Al_2O_3 ratio is not acceptable in MTP process because high ratio causes the presence of less active sites hence less acidity which results in a drop of methanol conversion which can be seen with HZ-410, therefore there should be an appropriate ratio of strong and weak acid sites to enhance propylene production.

Table 4.9 Conversion, Selectivity and Yield results for ZSM-5 catalyst with different SiO_2/Al_2O_3 ratio.

SiO_2/Al_2O_3	**30**	**50**	**80**	**280**	**410**
Conversion (%)	100	98	98	100	88
Selectivity (%)					
C_1	9.1	8.4	8.6	0.3	0
C_2^-	2.3	2.0	0.8	0.2	0.1
$C_2^=$	18.1	18.2	15.6	11.8	10.8
C_3^-	9.1	6.6	3.4	2.1	1.4
$C_3^=$	**21.6**	**27.6**	**37.8**	**47.3**	**49.2**
$C_4^=$	9.9	10.7	18.7	28.7	31.1
$C_{4\text{-}5}$	29.9	26.5	15.1	8.0	6.4
$C_{5+}^=$	0	0	0	1.6	1.0
$C_3^=/ C_2^=$	1.2	1.5	2.4	4.1	4.6
Yield (%)					
$C_2^=$	4.6	4.4	3.8	3.1	4.9
$C_3^=$	**8.3**	**10.0**	**13.0**	**17.4**	**16.4**
$C_4^=$	5.1	5.1	9.2	14.0	9.7
Aromatics	8.0	6.3	4.0	2.4	1.7

Reaction conditions: T=500 °C, P= 1bar, WHSV=15 h^{-1}, time of stream 2.5 hours.

4.2.6 Catalytic Performance of Synthesized FeHZSM-5 Catalysts

FeHZSM-5 catalysts with SiO_2/Fe_2O_3 molar ratio of 80, 100 and 150 were synthesized by the method discussed in section 3.1.4. The catalytic activity of these samples was carried out at optimized process conditions i.e. temperature 500 °C, pressure 1 bar and space velocity 15 h^{-1}. The results are tabulated in Table 4.10, from the results obtained it can be seen that the catalyst with SiO_2/Fe_2O_3 ratio 100 has better performance which results in methanol conversion 95% and propylene selectivity 46% and yield 17.1%. Drop in methanol conversion for high ratio FeZSM-5-150 catalyst was observed. This drop in methanol conversion is due to the low acidity of the catalyst. High yield of aromatics was observed in FeHZSM-5 zeolite catalysts comparing to HZSM-5 zeolite catalysts, the reason for this is that presence of iron as an active site in FeHZSM-5 catalysts. Due to the presence of Fe the reaction follows ethylene pool cycle in hydrocarbon pool mechanism and hence there is more ethylene and aromatics formation in MTP process.

Table 4.10 Experimental results obtained for FeHZSM-5 at WHSV 15 h^{-1}.

SiO_2/Fe_2O_3	**80**	**100**	**150**
Conversion (%)	77	95	70
Selectivity (%)			
C_1	17.8	10.5	24.6
C_2^-	5.6	2.3	3.0
$C_2^=$	10.1	12.4	18.7
C_3^-	1.2	1.2	1.7
$C_3^=$	**39.0**	**46.0**	**34.5**
$C_4^=$	21.1	25.9	17.6
C_{4-5}	5.0	1.3	0
$C_{5+}^=$	0	0	0
$C_3^=/ C_2^=$	3.9	2.9	1.8
Yield (%)			
$C_2^=$	2.2	3.1	3.4
$C_3^=$	**12.7**	**17.1**	**9.5**
$C_4^=$	9.2	12.8	6.4
Aromatics	7.2	10.6	12.9
Water + DME	59.6	52.2	73.8
Mass Balance	94	97	95

Reaction conditions: T=500 °C, P= 1bar, WHSV 15 h^{-1} and time of stream 2.5 hours.

4.2.7 Selection of Best Catalyst for Further Improvement

From the observations presented in Table 4.9, with the increase in SiO_2/Al_2O_3 molar ratio of zeolites, propylene and butylene become predominant products in MTP. Figure 4.23 shows propylene selectivity and yield comparison of zeolite ZSM-5 with SiO_2/Al_2O_3 molar ratio of 30, 50, 80, 280 and 410. ZSM-5 with SiO_2/Al_2O_3 ratio of 280 was considered best which gave 47.3% propylene selectivity and 17.4% yield with 100% methanol conversion. For further improvements in our results we work on this catalyst and did modifications by using promoters and coating on macroporous monolith support.

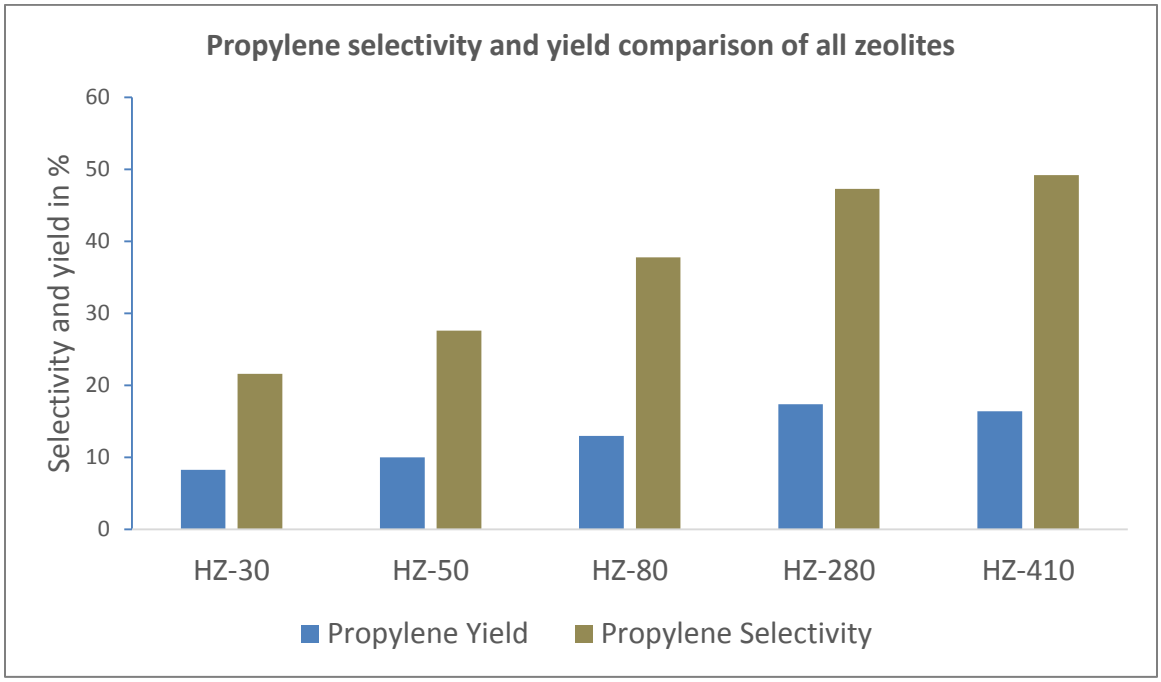


Figure 4.23 Propylene selectivity and yield comparison of all zeolite catalysts.

4.3 Effect of Promoters

Various promoters were incorporated into zeolite ZSM-5-280 catalyst using the impregnation method discussed in section 3.1.3**.** Modified zeolite catalysts were evaluated in the reactor at optimized conditions discussed in section 4.2.4 & 4.2.5. Best modified catalysts were characterized by various characterization techniques discussed in section 4.1. Promoters loading amount was varied to get the best performing catalyst.

4.3.1 ZSM-5-280 Modification

HZ-280 was considered as the best performing catalyst in terms of SiO_2/Al_2O_3 ratio which result in high methanol conversion, propylene selectivity and yield. This catalyst was further modified with phosphorus (P), cerium (Ce), iron (Fe) and lanthanum (La) by incipient impregnation method. Impregnation on high SiO_2/Al_2O_3 ratio catalyst is rarely reported in the literature. Catalyst activity test was carried out at temp 500 °C, 1bar pressure, and WHSV of 15 h^{-1}. It is a well-known fact that loading of promoters on zeolite has both positive and negative effect on results [50]. Since acidity is a key factor for the formation of various hydrocarbons in MTP reaction, therefore, there is a need to adjust the ratio of weak to strong acid sites to get more desired product which can be done by using appropriate promoters [49], [51].

Table 4.11 shows the effect of P, Ce, Fe and La on HZ-280 catalyst with optimized loading and on optimum reaction conditions. Phosphorus loading was done in three amount 0.1, 0.2 and 0.5 wt%, Cerium was loaded with 0.3, 0.5 and 1.0 wt%, and iron was loaded with 0.2 and 0.4 wt% while lanthanum was loaded with 0.5 and 1.0 wt%. The effect of

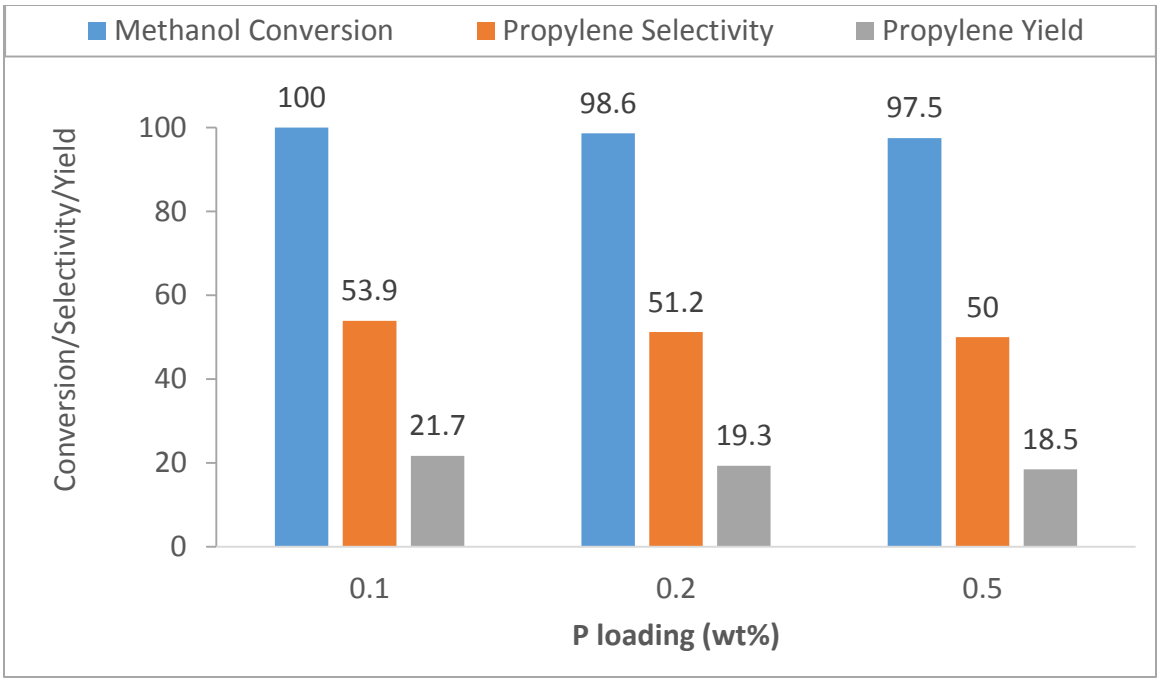
loading of these promoters are shown in Figure 4.24 and Figure 4.25, with the increase in loading there is a drop in methanol conversion, propylene selectivity and yield. This drop is due to much decrease in acidity of the catalyst. From the results tabulated in Table 4.11, it is clear that all four promoters increase propylene selectivity. For all these promoters loading was optimized because of high loading cause a negative effect on the results, this is due to the reason that high loading decreases the amount of acid sites present in HZ-280 catalyst. The decrease in active sites results in a drop of methanol conversion. Optimum loading amount for P, Ce, Fe and La obtained are 0.1, 0.5, 0.2 and 0.5 wt% respectively. A comparison graph is shown in Figure 4.26 for propylene selectivity and yield with optimum loading of promoters on HZ-280 catalyst.

0.1 wt% P loading on HZ-280 shows best results with 53.9% propylene selectivity and 21.7% yield while 0.5wt% Ce loading gave 50.7% propylene selectivity and 19.3% yield with 100% conversion. Selectivity of olefins for modified catalysts are increased for all these four promoters comparing to parent HZ-280 catalyst. There is an increase in selectivity of ethylene with Ce, Fe and La which agrees hydrocarbon pool mechanism [13], [110]. Methylbenzene and alkene are two HC's pool cycles according to this mechanism which is discussed in section 2.6.1. Formation of more ethylene reflects HC's formation follows the alkene pool cycle. While P loading results indicate that the HC's formation follows methylbenzene pool cycle, therefore, there is a substantial decrease in aromatics due to dissociation of polymethyl benzenes. The decrease in aromatics causes slow deactivation of the catalyst.

Table 4.11 Conversion, Selectivity and Yield results for parent and Modified HZ-280 catalyst.

Promotor	Parent	P	Ce	Fe	La
Amount (wt %)	0	0.1	0.5	0.2	0.5
Conversion (%)	100	100	100	100	100
Selectivity (%)					
C_1	0.3	0.1	1.2	0.3	0.3
C_2^-	0.2	0	0.6	0.2	0.2
$C_2^=$	11.8	10.9	14.6	13.2	14.6
C_3^-	2.1	1.5	1.8	2.5	2.3
$C_3^=$	**47.3**	**53.9**	**50.7**	**49.1**	**48.5**
$C_4^=$	28.7	29.4	26.4	28.5	27.5
C_{4-5}	8.0	3.7	4.0	6.2	6.4
$C_3^=/ C_2^=$	4.1	5.0	3.5	3.7	3.4
Yield (%)					
$C_2^=$	3.1	2.9	3.5	3.3	3.5
$C_3^=$	**17.4**	**21.7**	**19.3**	**18.4**	**18.2**
$C_4^=$	14.0	15.7	13.4	14.3	14.1
Aromatics	2.4	1.0	1.9	1.5	1.7

Reaction conditions: T=500 °C, P= 1bar, WHSV=15 h^{-1}, time of stream 2.5 hours.



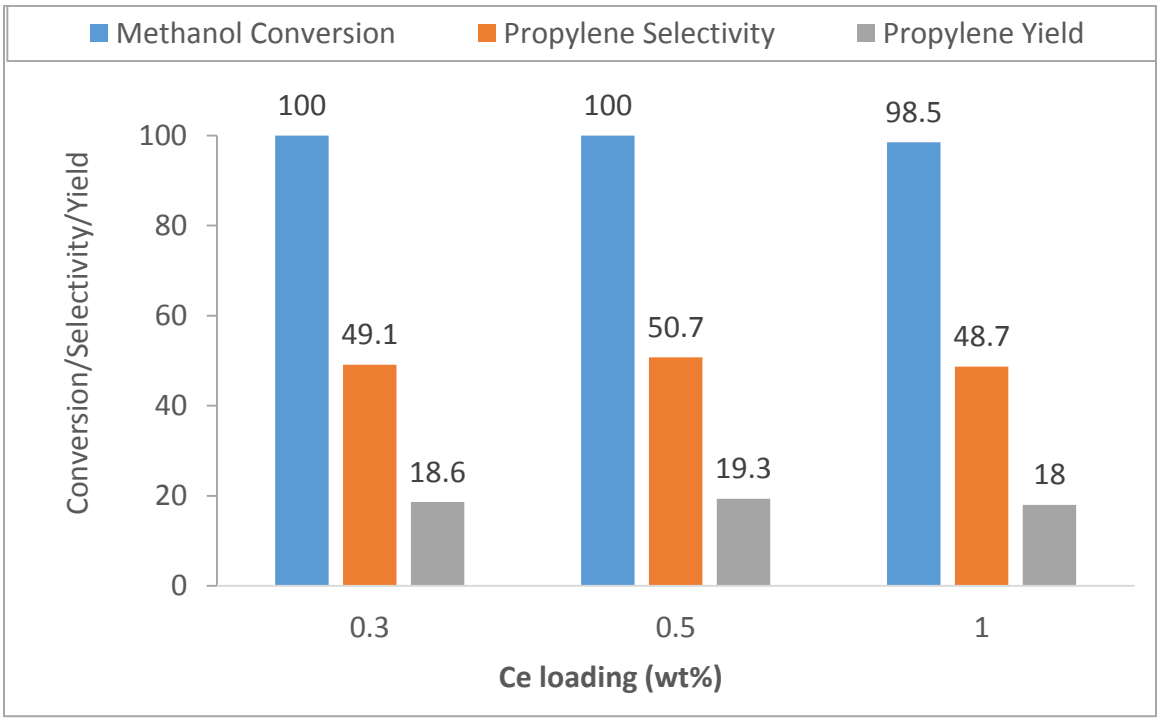


Figure 4.24 Methanol conversion, propylene selectivity and yield comparison for P and Ce modified HZ-280 catalysts.

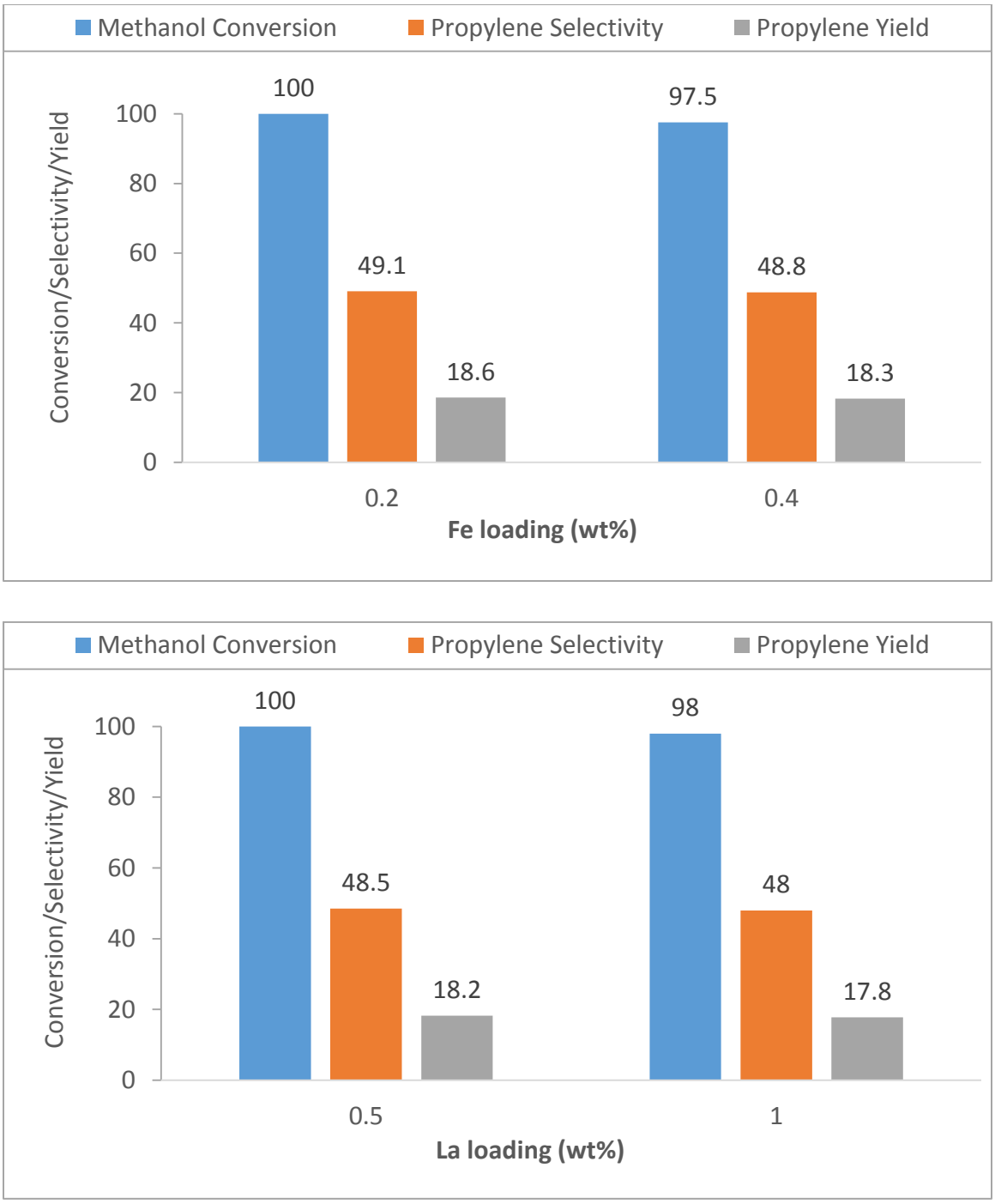


Figure 4.25 Methanol conversion, propylene selectivity and yield comparison for Fe and La modified HZ-280 catalysts.

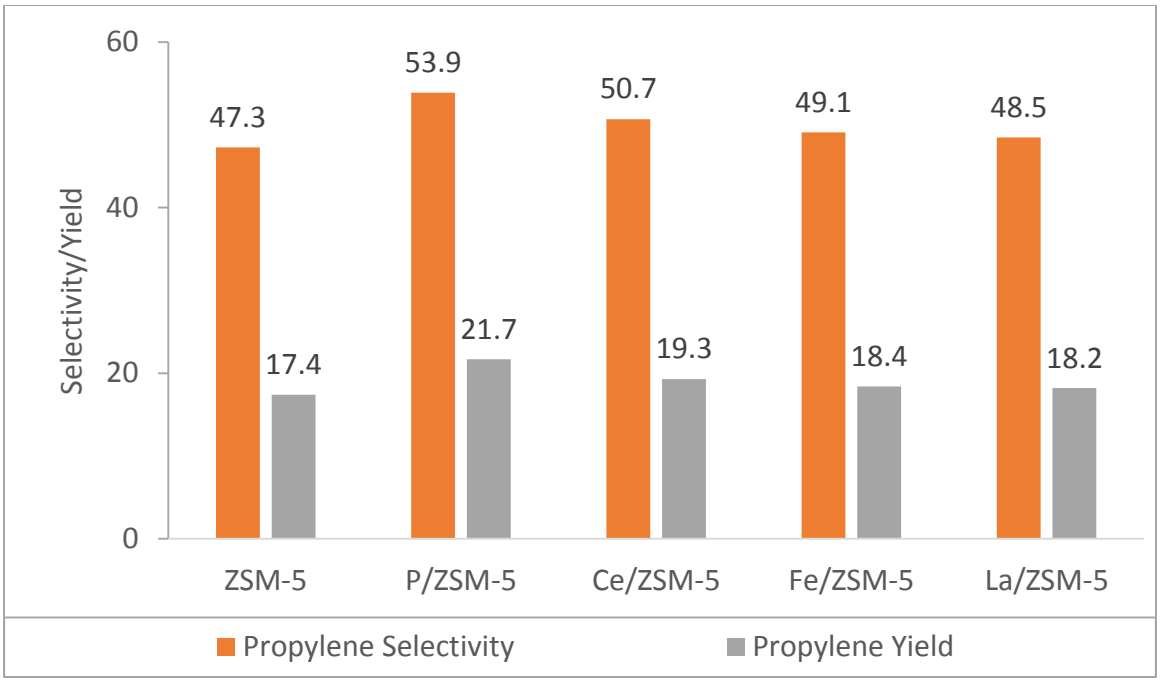


Figure 4.26 Propylene selectivity and yield comparison for parent and modified HZ-280 catalysts.

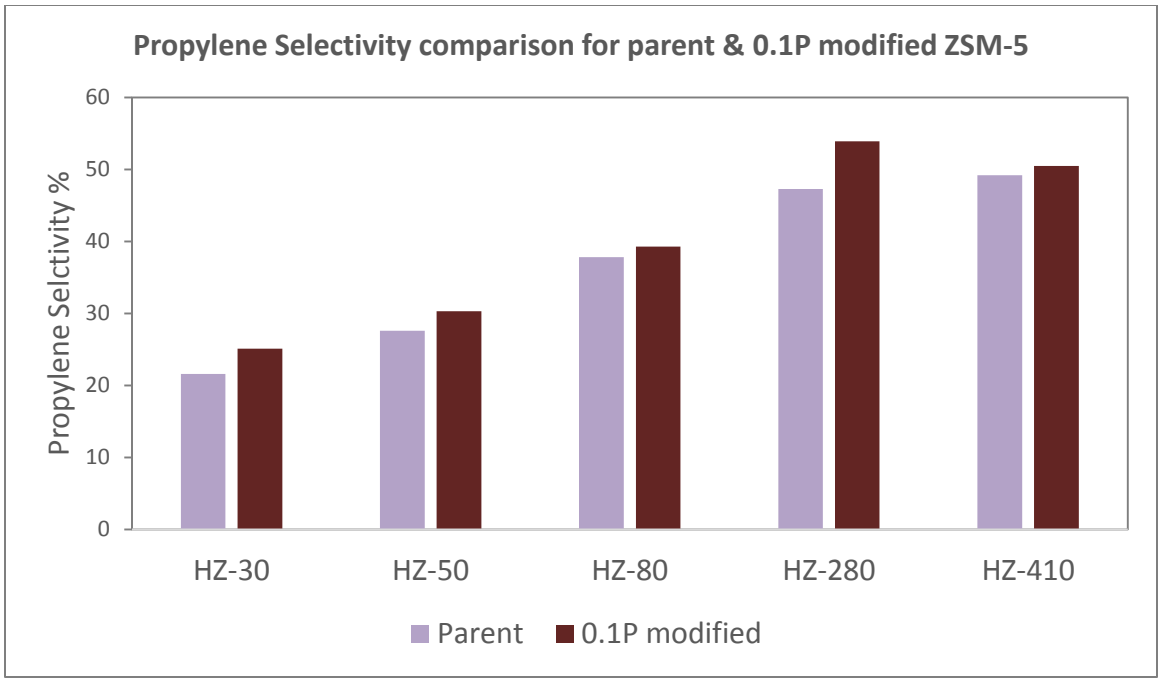
4.3.2 Effect of 0.1 wt% P loading on other zeolites ZSM-5 Catalysts

Phosphorus loading on HZ-280 catalyst effectively improves propylene selectivity and yield. 0.1 wt% P loading was done on other zeolites i.e. HZ-30, 50, 80 and 410 to check if it makes any improvements to other samples. Table 4.12 shows the catalytic activity of 0.1 wt% P loaded zeolites with different SiO_2/Al_2O_3 ratio. By comparing the results of Table 4.9 and Table 4.12 it is very clear that phosphorus modification improves the olefins selectivity especially selectivity of propylene and yield for all zeolite catalysts. P modification on HZ-410 increases the methanol conversion to 7%. There is an extensive decrease in aromatics and alkanes which is due to the elimination of strong acid sites. The improvement in propylene selectivity and yield is shown in Figure 4.27.

Table 4.12 Conversion, Selectivity and Yield results for 0.1 wt% P-modified other zeolites.

SiO_2/Al_2O_3	**30**	**50**	**80**	**410**
Conversion (%)	100	100	100	95
Selectivity (%)				
C_1	7.0	6.5	5.1	0
C_2^-	2.1	1.0	1.2	0
$C_2^=$	15.9	14.9	12.3	8.2
C_3^-	12.5	7.3	4.1	2.0
$C_3^=$	**25.1**	**30.3**	**39.3**	**50.5**
$C_4^=$	10.9	21.3	22.3	32.3
C_{4-5}	26.5	18.7	15.7	4.2
$C_3^=/ C_2^=$	2.0	2.4	3.4	6.0
Yield (%)				
$C_2^=$	3.6	3.3	3.0	2.0
$C_3^=$	**10.0**	**11.9**	**14.4**	**17.2**
$C_4^=$	5.8	10.5	10.9	10.2
Aromatics	7.1	5.1	2.9	1.1

Reaction conditions: T=500 °C, P= 1bar, WHSV=15 h^{-1}, time of stream 2.5 hours.



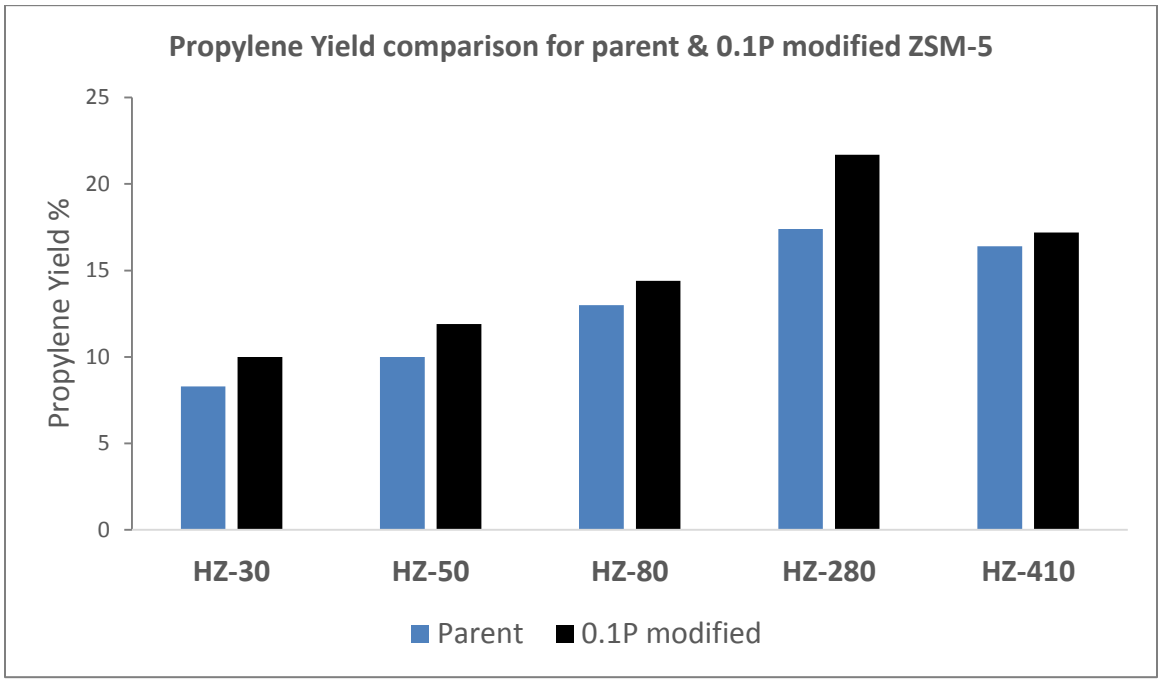


Figure 4.27 Propylene selectivity and yield comparison for parent and P-modified HZ-30, 50, 80 and 410.

4.4 Monolith coated Catalyst Evaluation

The best catalyst obtained in the study was ZSM-5 with SiO_2/Al_2O_3 ratio 280, this catalyst was coated on monolith for further improvements in results. Monolith structured catalyst was prepared by dip coating method discussed in section 3.1.5**.** The catalyst was evaluated at 500 °C, 1bar pressure, and WHSV=15 h^{-1}. The characterization results have been discussed earlier in section 4.1.

Experimental results obtained are tabulated in Table 4.13 which shows that there is an increase in propylene selectivity and yield by coating on the monolith. Propylene selectivity 56.4% with 100% conversion was obtained with single layer zeolite HZ-280 coating (6.8%) on the monolith. Increasing the amount of zeolite coating by double layer and triple layer coating on monolith support result in a drop of methanol conversion. With the increase in zeolite coating by double layer and triple layer, the drop in methanol conversion is due to resistance created by product species inside the monolith channel, this resistance offer intra pore diffusion limitations to the reactant species. Radial diffusion of reacting species is dominating inside the monolith catalyst channels than the vertical axial diffusion which is dominating in the catalyst packed bed reactor system.

This increase in propylene selectivity for single layer monolith catalyst compared to packed bed catalyst is due to better mass and heat transfer performance, low-pressure drop and contact time due to shorter diffusion distance and faster intra-diffusion rate of both reactants and products inside the monolith channels. By comparing results in Table 4.9, 4.11 and 4.13 it is clear that monolith structured catalyst has an advantage over pelletized packed bed catalysts. From the SEM images obtained the zeolite coating thickness for single layer

monolith catalyst was obtained to be 4.2 μm. Figure 4.28 reflects the effect of zeolite single layer, double layer and triple layer coating on propylene selectivity and yield.

Single layer ZSM-5-280 monolith coated catalyst was also modified with 0.1 wt% phosphorus in an expectation of further improvement in olefins selectivity especially propylene but P loading causes a negative effect. The results are shown in Table 4.13, the reason for this negative effect is that in absence of aromatics more cracking of higher olefins was happening in the intra pores of the zeolite catalyst. This cracking causes coke formation due to which the deactivation rate of this catalyst was fast. The conversion was 98.0% based on 2.5 hours run while conversion drops to 4% after 8.5 hours. Due to this reason, the performance of this catalyst was regarded poor.

Table 4.13 Effect of zeolite HZ-280 coating on monolith.

	Single layer	Double layer	Triple layer	0.1P Single layer
Wt. of zeolite (gm)	0.38	0.56	0.71	0.38
Coating (%)	6.8	10.3	13.1	6.8
Conversion (%)	100	98.0	94.3	98.0
Selectivity (%)				
C_1	0	0	0	0
C_2^-	0	0	0	0
$C_2^=$	8.1	8.9	9.3	7.6
C_3^-	1.1	1.3	1.7	0.94
$C_3^=$	**56.4**	**53.6**	**50.9**	**57.9**
$C_4^=$	30.2	30.1	26.8	24.7
C_{4-5}	4.2	6.1	10.1	4.9
$C_3^= / C_2^=$	7.0	6.0	5.5	7.6
Yield (%)				
$C_2^=$	2.2	2.3	2.5	1.9
$C_3^=$	**23.4**	**22.5**	**20.1**	**22.4**
$C_4^=$	16.8	15.7	12.9	14.7
Aromatics	0	0	0	0
Water + DME	52.0	52.5	52.5	52.5
Mass Balance (%)	98.0	97.5	95.2	96.0

Reaction conditions: T=500 °C, P= 1bar, WHSV=15 h^{-1}, time of stream 2.5 hours.

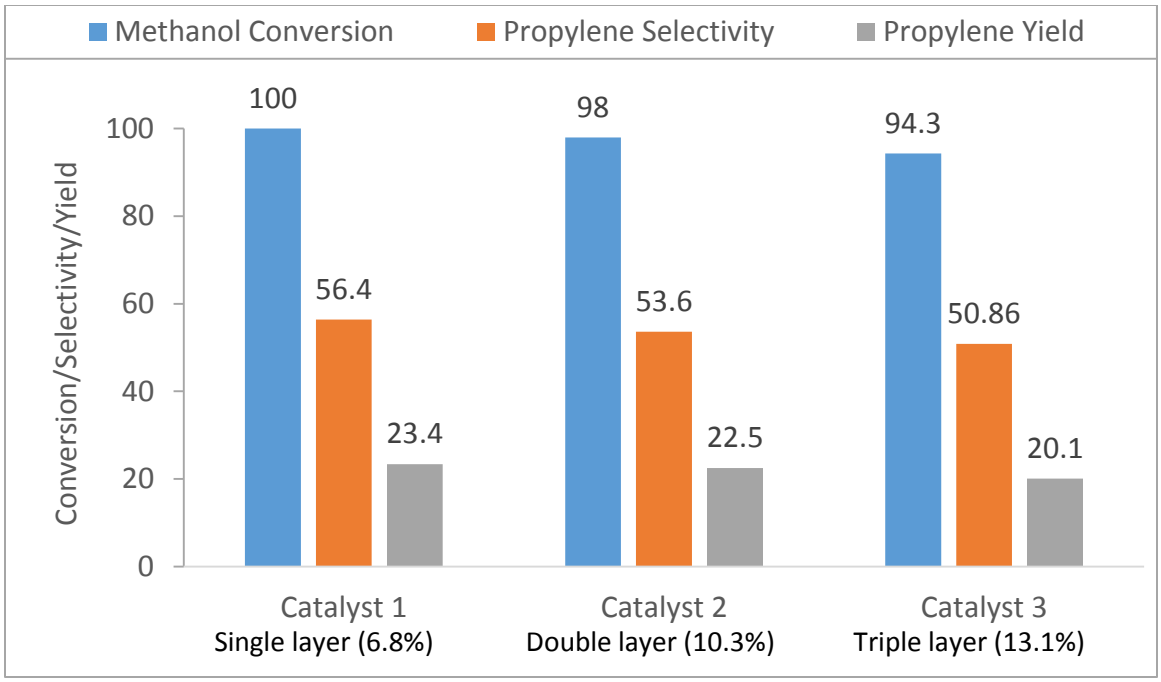


Figure 4.28 Propylene selectivity and yield comparison for HZ-280 coated on the monolith.

4.5 Stability Tests

The catalyst performance for methanol conversion, propylene selectivity and yield of aromatics as a function of time is shown in Figure 4.29 and Figure 4.30 Starting with 100% methanol conversion HZ-280 coated monolith catalyst remains stable with methanol conversion 82% after 41.5 hours while conversion drops by 33% and 24% for parent and P-modified catalysts. Propylene selectivity improves significantly from 47.3% to 53.9% and 56.4% for parent, P-modified and single layer monolith coated catalysts. Olefins selectivity and yield comparison have been shown in Figure 4.31. It is a well-known fact that the catalyst deactivation is due to coking in MTP process [111]. The rate of drop in methanol conversion was more in the parent catalyst due to more formation of aromatics in the product stream. The dearomatization was maximum in monolith catalyst than P-modified catalyst due to polymethyl benzene route of hydrocarbon pool mechanism [13], [110] in which polyaromatics dissociate into olefins which improve propylene selectivity to a great extent. Due to no aromatics generation in monolith catalyst, the rate of drop in conversion was slow as compared to the parent and P-modified catalysts.

Monolith Structured catalyst best results are due to the advantage of monolith structured support which provides better mass and heat transfer performance, low-pressure drop and contact time due to shorter diffusion distance and faster intra-diffusion rate of both reactants and products. The ZSM-5 coated monolith structured catalyst results revealed that these catalysts are the benchmark for the conversion of methanol to light olefins.

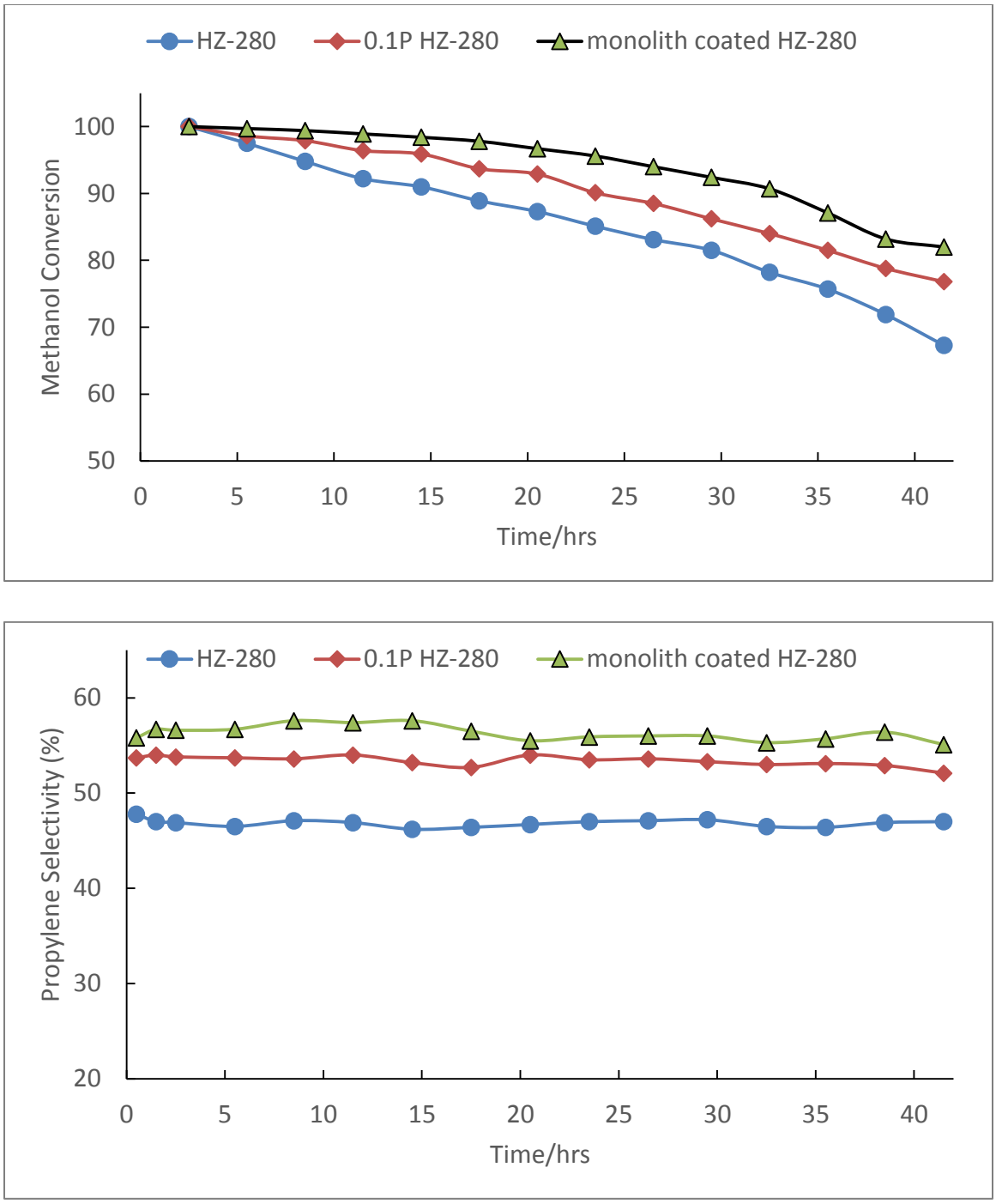


Figure 4.29 Comparison of methanol conversion and propylene selectivity for HZ-280, 0.1P HZ-280 and single layer monolith coated HZ-280 catalysts.

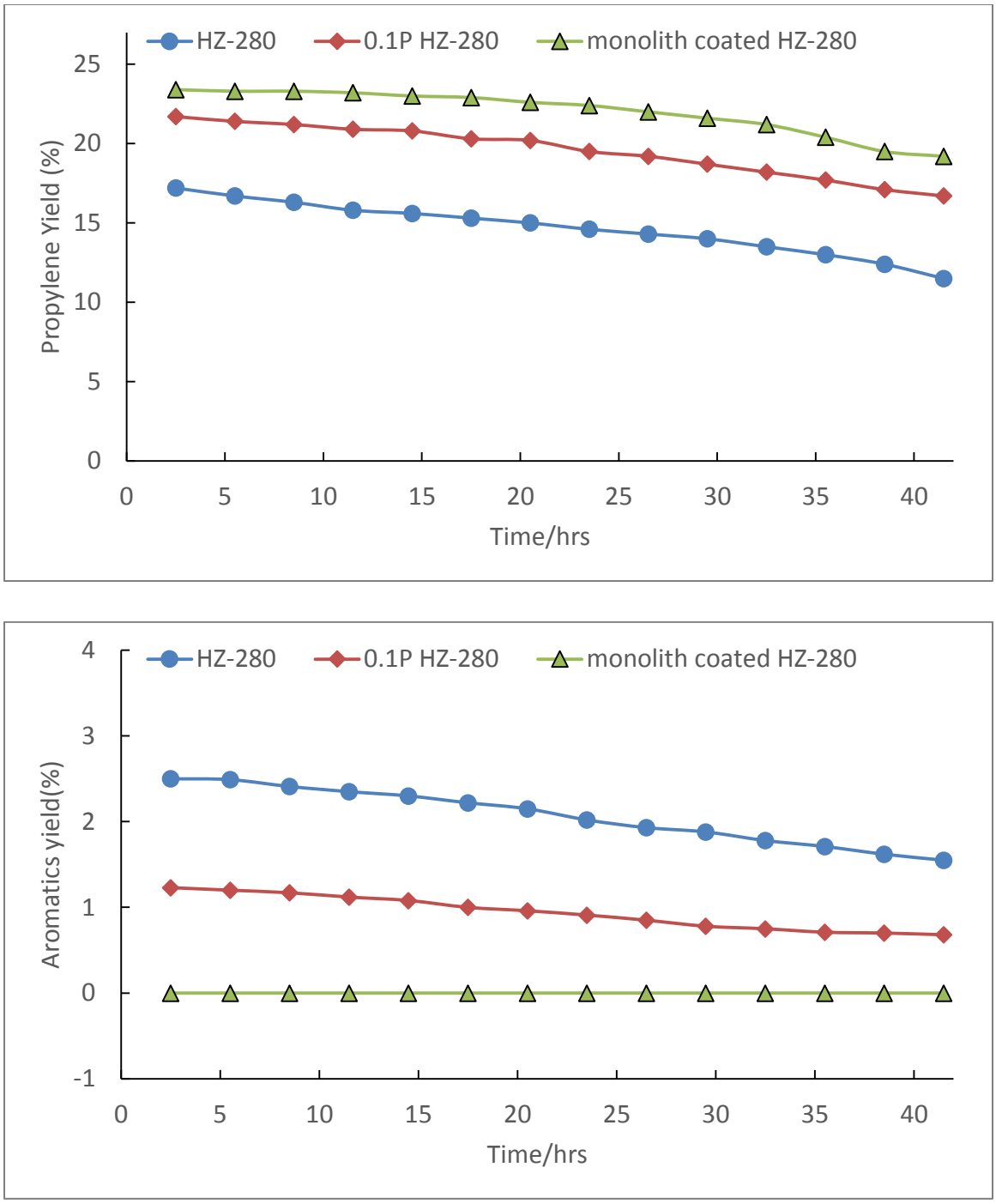
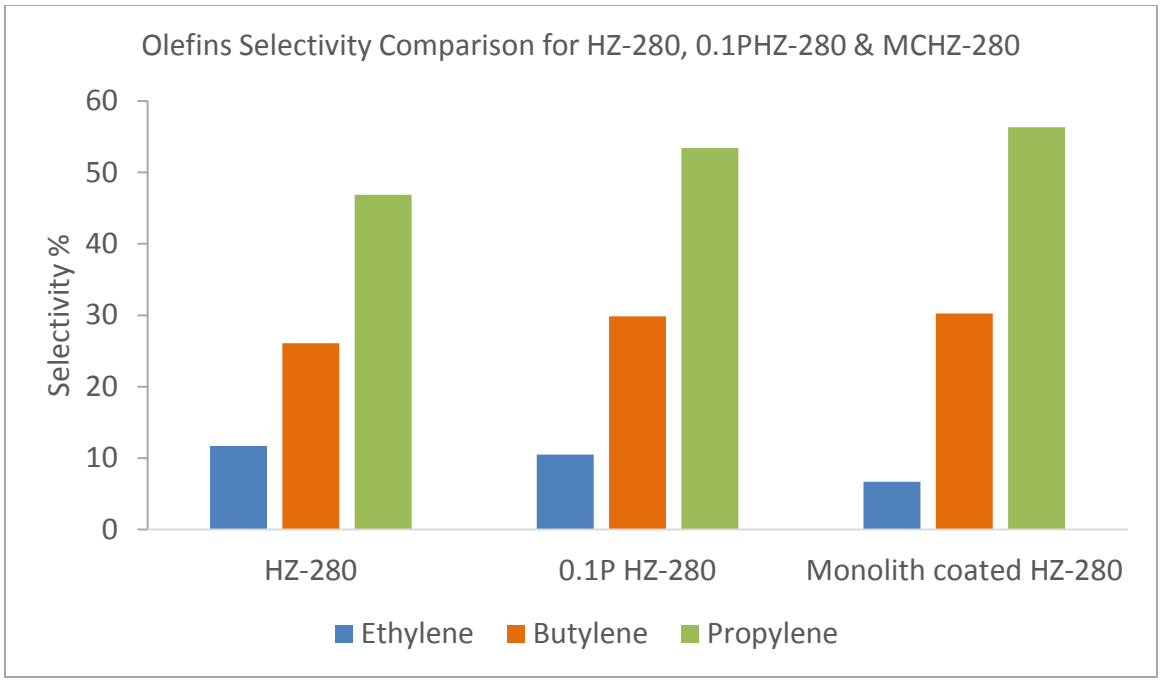


Figure 4.30 Comparison of propylene and aromatics yield for HZ-280, 0.1P HZ-280 and single layer monolith coated HZ-280 catalysts.



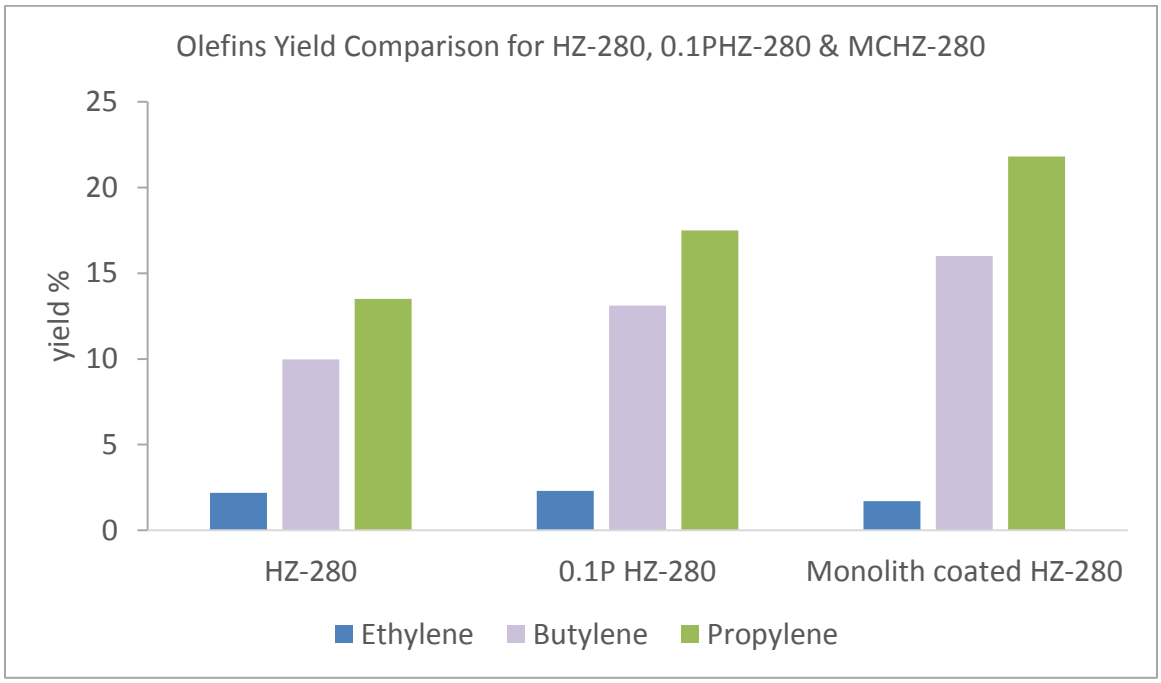


Figure 4.31 Olefins selectivity and Yield comparison for HZ-280, 0.1P HZ-280 and single layer monolith coated HZ-280 catalysts.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Methanol conversion to propylene was conducted in a fixed bed reactor system using zeolite, modified zeolite and monolith coated zeolite catalysts. Following are important conclusions drawn:

- Pelletized zeolites ZSM-5 with different SiO_2/Al_2O_3 ratio were evaluated for the best catalyst at optimized reaction condition i.e. temp 500 °C, 1 bar pressure and WHSV of 15 h^{-1}. Zeolite ZSM-5 with SiO_2/Al_2O_3 molar ratio 280 showed best results for methanol conversion 100%, propylene selectivity 47.3% and yield 17.4%.
- Effect of promoters P, Ce, Fe and La on zeolite ZSM-5-280 were also examined and concluded that all of these promoters have positive effect on propylene selectivity, 0.1 wt% phosphorus has effectively increase the propylene selectivity by 14.0% and yield by 24.7% with 100% methanol conversion. This improvement was due to partial removal of strong acid sites and reduction in average pore diameter of modified catalyst.
- The single layer monolith coated structured catalyst with 6.8% ZSM-5-280 coating had shown a pronounced improvement by increasing propylene selectivity by 19.2% and propylene yield by 34.5% with 100% methanol conversion. There was a drop in

methanol conversion and propylene selectivity in double layer and triple layer monolith coated ZSM-5-280 catalysts.

- The zeolite coating thickness for single layer, double layer and triple layer monolith coated HZ-280 catalysts were obtained to be 4.2 µm, 6.8 µm and 10.4 µm.
- Zeolite coating on monolith support reduces aromatics generation to 0% in MTP reaction and hence produce more olefins and remains stable with 82% conversion after 41.5 hours.

The results obtained in the study indicate that honeycomb monolith structured catalyst has an advantage over traditional packed bed catalyst in MTP process. This improvement is due to better mass and heat transfer performance and low pressure drop due to micron size catalyst bed in monolith structured catalyst which results in less residence time which causes decoupling of intrinsic reactions and hence more olefins production in MTP process.

5.2 Recommendations

- Water co feeding with methanol can be studied.
- Other structured supports like metallic monolith SiC foams can be prepared and the results can be compared with monolith structured catalyst.
- Investigate the effect of nanocrystal size zeolite ZSM-5 and compare its results with micron crystal size zeolite ZSM-5 catalysts.
- Use in-situ hydrothermal crystallization method for structured catalyst preparation.
- Modeling of honeycomb monolithic reactor vs packed bed reactors can be done for further analysis.

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